REQ. NO. 3-9121

Final Report

for

EMR Contract OST83-00132

on

SURFACE CHARACTERIZATION RELEVANT TO ENERGY RESOURCES PROCESSING

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April 1984

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179 pp

TABLE OF CONTENTS

Page

INTRODUCTION 1

EXPERIMENTAL TECHNIQUES 3

1. Adhesion Technique 3
2. Sedimentation Technique 7

STUDY No. I: "Surface Properties of Coal Particles in Aqueous Media. I. Solidification Front Measurements" I 1-20

STUDY No. II: "Surface Properties of Coal Particles in Aqueous Media. II. Adhesion of Coal Particles to Polymeric Substrates" II 1-33

STUDY No. III: "Surface Tension Effects in the Sedimentation of Polymer Particles in Various Liquid Mixtures" III 1-27

STUDY No. IV: "Surface Tension Effects in the Sedimentation of Coal Particles in Various Liquid Mixtures" IV 1-50

APPENDIX A: Solidification Front Experiments for Coal Samples in an Organic Medium A 1-14

APPENDIX B: Supplementary Sedimentation Volume Measurements for Coal Samples B 1-5

APPENDIX C: Determination of the Surface Tension of Pure Liquids and Binary Liquid Mixtures C 1-12

INTRODUCTION

The ability to predict, control and monitor the wettability, the floatability and the adhesion of coal particles in various coal dispersions is of great importance in coal beneficiation processes and it requires a knowledge of the surface properties of the coal powders. Since coal fines may be dispersed either in organic or aqueous media during transportation and utilization, a study of the surface behaviour of coal in both types of media is of immediate concern in coal processing.

The purpose of the present contract work was to characterize the surface tension and the stability of dispersions of coal powders originating from both Western and Eastern Canada. Towards this end, three techniques, i.e. the advancing solidification front, the particle adhesion and the sedimentation volume techniques, were developed for and applied in the determination of the surface tension of coal particulate matter.

The major results of the present work are described in detail in the four manuscripts (submitted for publication) which form the body of this report. These studies are briefly discussed below. In Study No. I, the dualistic behaviour of the coal surface, as determined by the advancing solidification front method, is discussed. It was observed that the surface tension of coal particles varies with the nature of the suspending liquid medium, i.e. coal is hydrophobic in organic liquids and hydrophilic in water.

Results from the adhesion of coal to polymeric substrates in both organic and aqueous media are summarized in Study No. II.

Studies No. III and No. IV are concerned with the sedimentation behaviour and with the suspension stability of coal and polymer particles. Sedimentation volume experiments with well characterized polymer powders are prerequisite for a better understanding of the complexities observed in coal sedimentation. The results regarding polymer sedimentation in organic liquids are described in Study No. III, while the major results obtained from the sedimentation measurements of different coal samples are summarized in Study No. IV.

The experimental and technical details of the adhesion and sedimentation volume techniques that were developed for and applied in the measurement of the surface tension of coal are provided in the present report under Experimental Techniques, in addition to being included with the study concerned. The solidification front method, as it applies to organic media, was described previously; the same technical details regarding the application of the technique in an aqueous medium are given in Study No. I.

Supplementary results, not described in the four main studies, are summarized in the Appendices. In Appendix A, the surface properties of various coals, obtained by means of the solidification front technique in an organic medium, are discussed. Results of sedimentation volume measurements of coal samples, not previously considered, are given in Appendix B. Finally, a summary of the surface tension of liquids and liquid mixtures used for sedimentation volume studies are presented in Appendix C.

EXPERIMENTAL TECHNIQUES

In the interest of clarity and for the purpose of easy reference, two of the three techniques (adhesion and sedimentation volume) used in the determination of the surface tension of solid particulate matter are described here. The third technique (advancing solidification front) is described, in detail, elsewhere (see Study No. I).

1. Adhesion Technique

This technique relies on a quantitative evaluation of the extent of particle interaction with various polymer substrates of different surface tensions, γ_{SV}, when the particles are suspended in binary liquid mixtures with a wide range of surface tensions, γ_{LV}.

The -400 mesh fraction of each dry screened coal sample was infrasized on a Mark II infrasizer (which is essentially an air elutriation device). After the infrasizing process, the coal samples had a major dimension ranging from 1 to 20 μm. The coal powders were stored under vacuum in well sealed bottles protected from light at room temperature.

The polymer substrates (fluorinated ethylene propylene co-polymer (FEP), polystyrene (PS), low density polyethylene (LDPE), polyethyleneterephthalate (PET) and sulfonated polystyrene (SPS)) to which the coal particles adhered, were prepared by pressing strips of the polymers between glass microscope slides (cleaned with chromic acid) in a hydraulic heat press (except for polystyrene and sulfonated polystyrene which are already available as smooth, thin films). Immediately prior to use, the films were sonicated in analytical grade ethanol and rinsed in deionized distilled water.

The surface tension, γ_{LV}, of the suspending liquid mixtures was varied by employing different volume ratios of the two constituent liquids. The mixtures were chosen so as to cover a relatively wide range of liquid surface tensions. It should be emphasized that due to evaporation, the concentration and thus the surface tension of the liquid mixtures may change. The critical parameter is the surface tension of each mixture which was measured by means of the Wilhelmy balance technique immediately prior to the formation of the coal suspension in order to obviate the aforementioned problem.

The coal powders at a concentration of 1 mg/ml of solution were mixed in Erlenmeyer flasks on a shaker for 30 minutes. Thereafter, 0.5 ml of the coal suspension was placed on the various polymer surfaces. The suspensions were retained in 9 mm diameter holes formed in teflon blocks. To prevent leakage, the base of each hole was sealed with a medical grade Silastic gasket and the blocks were clamped under pressure to the polymer surface. There were three holes per block. Duplicate samples were used for each surface for each experimental condition.

The top of each hole was sealed with Parafilm to prevent evaporation. Thereafter, the systems were incubated at room temperature for three days. Then the teflon blocks were removed whilst the Silastic gaskets remained, thereby leaving a thin layer of liquid over the adherent particles, thus preventing exposure to an air interface. (This step is not trivial and is necessary in order to obtain interexperiment reproducibility of the data). The test surfaces were then rinsed with water under standard conditions in order to remove non-adherent particles. Standardization of the rinsing procedure was achieved by using a Bodine motor (Bodine Electric Co., Chicago, Illinois, U.S.A.), the shaft of which was attached through a 2-bar linkage to a slide holder which moves through the rinsing medium in a horizontal direction. The motor has associated with it a speed controller. The rinsing period, velocity and path length of the rinsing motion can all be controlled and thus it is possible to rinse simultaneously all of the polymer surfaces under identical conditions and therefore to compare directly the experimental results obtained.

Following rinsing, the surfaces were analyzed in order to determine the extent of particle adhesion per unit surface area. This was achieved by employing an automatic computerized digital image analysis system (Omnicon 3000, Bausch and Lomb, Rochester, N.Y.) attached to a Leitz Orthoplan microscope and using a 32X long working distance objective. The major advantage of this system is that the analysis is performed using a preprogrammed automatic stage motion control and accordingly, all operator bias and elements of subjectivity, as to which microscopic fields and how much surface area is examined, is completely removed. In this manner, it is possible to quantify rapidly the extent of particle adhesion to each of the polymer surfaces under the various experimental conditions. In view of the particle size heterogeneity and since, in several instances, particles touched one another, it was decided that the extent of particle adhesion to the substrate would be quantified by measuring the surface area covered by the particles and expressing this as a percentage of the total polymer surface area examined. For each experimental condition, the data from each of the six areas/polymer surface were summed in order to permit detailed statistical analysis. Which surface regions were analyzed was dictated by the automatic stage motion option which, since it operates in a rectilinear two-dimensional pattern, necessitated the choice of the largest square which could be fitted inside the circular area. Thus 67% of the surface area of each of the six areas per substrate material was examined. This rectilinear motion has the added advantage that it requires the exclusion of those areas in close proximity to the teflon walls forming the hole, thereby avoiding any "wall effects".

The percentage of the area occupied by the adhering coal particles from each suspension is plotted against the solid/vapour interfacial tension, γ_{SV}, of the polymer substrates. The resulting straight lines have different (negative as well as positive) slopes corresponding to the different surface tensions, γ_{LV}, of the suspending liquid mixtures. Finally, the slopes of the straight lines (% area/mJ/m^2) are plotted versus the liquid/vapour interfacial tension, γ_{LV}, of the suspending liquids. The slope becomes equal to zero at a value of γ_{LV} characteristic of the surface tension, γ_{PV}, of coal particles, thereby allowing one to experimentally determine the surface tension, γ_{PV}, of the adhering particles.

2. Sedimentation Volume Technique

The sedimentation volume, V_{sed}, of a powder can be determined in binary mixtures of non-polar as well as polar liquid combinations. The liquid mixtures are chosen such that the surface tension, γ_{SV}, of the solid particles (coals, polymers) falls between the surface tensions of the two constituent liquids.

There are several conditions which the suspending liquids must satisfy in order to be used for the sedimentation volume experiments. The criteria for choosing the liquid components are: (1) they should be chemically inert with respect to the solid particles and should not dissolve the particles or components thereof; (2) the boiling temperature should be reasonably high to minimize evaporation; (3) the density of the liquids should be lower than that of the particles; (4) liquids with a zero or nearly zero dipole moment as well as those with a higher dipole moment should be used to cover a wide polarity range; (5) the liquid components should be miscible with each other in all ratios; and (6) the surface tension, γ_{LV}, of the liquid mixtures should cover the surface tension range required.

For the sedimentation experiments performed with polymer powders, the liquid combinations were selected according to the aforementioned criteria. In the case of coal sedimentation, however, the first criterion might not be easily satisfied.

Chemically, coal is considerably more complex and heterogeneous than polymers and less resistant to organic liquids. Some components of coal can easily be dissolved by solvents; in some cases, such effects were experimentally observed as a discolouration of the supernatant liquid.

Prior to the actual sedimentation experiments, the powders were thoroughly agitated in the appropriate liquids in order to break up any aggregates and to displace air bubbles. For this purpose, a specified mass of a given powder was weighed into small polyethylene micro centrifuge tubes with tight fitting caps. The mass of powder used varied from 0.05 to 0.20 grams depending on the density, the particle size and the compactness of the powder. The sedimentation volume is defined as the volume occupied by the particles of a suspension after settling, expressed in ml per unit mass. In this series of experiments, since we are interested only in determining at which liquid/liquid combination the sedimentation extremum occurs, it is not necessary to employ exactly the same mass of powder in each case. It is the relative position of the V_{sed} extremum which is important, the absolute value of V_{sed} is not required.

The powder was weighed with analytical accuracy. The powders in the centrifuge tubes were then suspended in approximately 0.1 to 0.2 ml of the liquids with different compositions by agitating the samples for at least five minutes using a Vortex test tube mixer. In order to achieve complete displacement of air, the samples were left for 24 hours and then agitated again for another five minutes.

For the actual sedimentation experiments, graduated, 1 ml Wintrobe micro test tubes (100 mm high with an inner diameter of 3 mm) were used. These graduated tubes can be read to an accuracy of 0.001 ml.

Each of the dispersions prepared in the centrifuge tubes was then quantitatively transferred into the Wintrobe tube using Pasteur micropipettes. The selected liquid mixture was used as rinsing liquid in each case. Finally, the microtubes were filled up to a constant volume of 1.00 ml with the appropriate liquid mixture. The microtubes were then sealed and shaken for approximately five minutes so that the powder was totally and homogeneously suspended in the liquid column. The reading of the sedimentation volume, V_{sed}, of the coal or polymer powder was taken every day for three days to one week, depending on the sample, until no further change in V_{sed} occurred. This value of the sedimentation volume was recorded. Sedimentation volume was then plotted as a function of the surface tension, γ_{LV}, of the suspending binary liquid and the sedimentation extremum was determined.

STUDY No. I

SURFACE PROPERTIES OF COAL PARTICLES IN AQUEOUS MEDIA. I. SOLIDIFICATION FRONT MEASUREMENTS

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ABSTRACT

The particle/vapour interfacial tension of three types of coal in powdered form was determined by means of the solidification front technique in organic as well as aqueous media. The results obtained from experiments performed in organic media show that the three types of coal have an intermediate hydrophobicity in the surface tension range of 30-40 mJ/m² at 20°C. However, in the presence of water the coal is markedly more hydrophilic with a surface tension near that of water. This striking difference suggests that one and the same coal sample may have two effective surface tensions or even a range of surface tensions, depending on the suspending liquid. It appears that in water the coal particles acquire a thick hydration layer so that they are perceived by other phases present as "black water particles".

INTRODUCTION

The contact angle and surface tension properties of coal particles have been shown to be important parameters influencing processes such as coal washing, flotation and agglomeration.

In view of the potential importance of the wettability of coal powders in various technological processes, a number of methods have evolved which attempt to assess this parameter. These techniques include the sessile drop and captive bubble methods on sections or tablets of coal. Such approaches suffer from the fact that the final polished surfaces used for the measurement in many cases bear a questionable relation only to the coal in its actual or native state, partly because polishing removes surface layers and partly because of contamination with polishing powder and other contaminants. Secondly these methods necessitate fairly large pieces of coal which may not be available. But even if large pieces of coal are available they may, due to heterogeneity, such as inclusions of clay and other inorganic matter, not reflect properly the properties of small coal particles, even if these coals are generated from the very same large piece of coal.

In view of these difficulties we have recently studied wettability of coal particles [1,2] by means of a novel technique for the determination of contact angles on small, irregularly shaped particles [3-7]. In essence, the technique consists of a quantitative evaluation of the interaction of individual particles initially suspended in the melt of a suitably chosen matrix material, with the advancing solidification front of that material. We have previously described in detail both the theoretical basis of the technique [3,4] as well as its application in the determination of the surface tension of small polymer [3-7], and biological [8] particles. So far we have performed such measurements with coal particles only in organic matrix materials and found surface tension values of coal typically in the range of 30-40 mJ/m^2, corresponding to contact angles of water in the range of approximately 65-85° [1,2,9]. Actual contact angle measurements with water on polished sections of coal corroborate these results [10]. In this study we present the results of measurements of the surface tension of small coal particles obtained with the solidification front technique with water/ice as the matrix material rather than organic matrix materials.

MATERIALS AND METHODS

Apparatus

Particle interaction with the advancing solidification front is studied in a specially designed chamber which has been described in detail elsewhere [3,8]. In order to establish a suitable temperature gradient, the chamber is heated electrically at one end and cooled at the other end. The temperature gradient can be controlled accurately through the use of electronically controlled Peltier units.

Coal particles are placed in the chamber together with the matrix materials and then covered with a microscope coverslip. Both the chamber and the coverslip are carefully cleaned before each experiment in order to prevent contamination of the sample. The chamber is then mounted on the stage of the microscope. The cell is heated electrically to melt the purified matrix powder or, in the case of the water/ice system, is cooled to form the solidification front. The rate of advance of the solidification front can be controlled by adjusting the temperature programmer which regulates the temperature of the heating and cooling units.

The interaction between the particle and the solidification front is observed through a microscope using a long-working distance objective lens of 32X magnification employing either reflected or transmitted light, depending on the nature of the matrix material.

At low rates of solidification particles embedded in a melt may be either rejected or engulfed when encountered by the solidification front. The first and decisive step in particle engulfing is adhesion of the particle to the solidification front. Thermodynamically adhesion is governed by the free energy of adhesion

$$\Delta F^{adh} = \gamma_{PS} - \gamma_{PL} - \gamma_{SL} \qquad (1)$$

where

γ_{PS} is the particle/solid interfacial tension,

γ_{PL} is the particle/liquid interfacial tension, and

γ_{SL} is the matrix solid/liquid interfacial tension. Engulfment is expected when the free energy change in Eq. (1) is negative. When it is positive, rejection, i.e. pushing of the particle, by the solidification front takes place. However, as the rate of solidification increases viscous drag builds up and eventually overpowers the thermodynamic repulsion, leading to engulfment. The solidification front velocity at which this process occurs is called the critical velocity, V_c. It can be measured experimentally and correlated with the free energy of adhesion by means of a scheme of dimensional analysis [11]. Finally, the surface tension and contact angle information for the coal particles can be obtained through the equation of state approach [12].

Matrix Materials

For the present investigation two matrix systems were employed: (1) thymol, and (2) water.

Thymol was obtained from Eastman-Kodak (Rochester, N.Y.) and zone refined prior to use. The water used in this study was deionized and double distilled. Purity of the water was monitored by means of surface tension measurements using a Wilhelmy Balance Apparatus [13].

Coal

Three coal samples have been employed in this study: Devco Metallurgical, B.C. Coal and Coal No.3. The samples were provided by EMR, CANMET, Coal Research Laboratory, Edmonton, Alberta, Canada. The origin, rank, type of sizing and density of the three coal samples are given in Table 1. Following infrasizing on a Mark II infrasizer (which is essentially an air elutriation device), the coal samples were stored under vacuum in sealed bottles protected from light, at room temperature. The ground and fractionated coal powder had a wide spectrum of particle sizes ranging from 1 to 300 μm in diameter. A freezing front experiment with thymol as matrix material was performed over this complete particle size range. For one of the coals (Coal No.3), the experiments with water as matrix material were also performed over the complete size range. Since these results showed no size dependence, it was decided that experiments would be performed only for the smallest fraction of particles in the range from 1-20 μm in diameter for the two other coals.

The dimensional analysis which is used to derive the surface tension of the coal particles from the critical velocity, V_c, of engulfment requires a knowledge of a number of physical properties of the particles. These quantities, which need to be separately determined, are density, ρ_p, specific heat, C_p, and thermal conductivity, k_p, for each sample. The density of the coal samples was determined by means of sample volume measurements using a null pycnometer. Specific heat was determined using a Perkin-Elmer Model DSC-2 as described previously [14]. At the present time, there is no suitable technique to measure the actual thermal conductivity of different coal fractions, but an average thermal conductivity value was estimated as 1.214×10^{-2} (J/m·s·K) [15].

The thermal and physical properties of the two matrix materials and of the three types of coal particles are given in Table 2.

RESULTS

Figure 1 shows a typical plot of solidification front velocity *versus* particle diameter for B.C. coal particles in a thymol matrix, and in a water/ice matrix, for the narrow size fraction in Figure 2. The critical velocity is defined as the velocity which separates rejection and engulfment of particles. All our experiments show, however, that the transition from rejection to engulfment is not sharp, so that we prefer to specify three modes of particle behaviour [1-8]. At relatively high rates of advance, the particles are *engulfed* immediately on contact with the solidification front (mode 1). At intermediate rates, the particles are rejected through various distances before being engulfed (mode 2). At relatively low rates of solidification, a steady-state *rejection* of any individual particle was observed without engulfment (mode 3). The three modes of particle behaviour are represented in Figures 1 and 2 by different symbols. The upper line in these figures is drawn such that no further transition points, i.e. momentary pushing followed by engulfment, are found above this curve. The lower line is drawn so that no transition readings are found below this curve. This band thus represents the maximum possible error. The center line is the mean position between the upper and lower curves and is taken as the critical velocity, V_c, for each particle size.

Figure 3 is a composite figure showing the critical velocity, V_c, for the three types of coal as a function of particle diameter, D, obtained from the mean line of the experimental data band of detailed plots of the type given in Figures 1 and 2. The left hand side of Figure 3 gives the data for the thymol solidification front systems whilst the right hand side provides the data for the water/ice systems.

Table 3 provides a comparison of the critical velocity data and the resultant γ_{PV} values for the three coal specimens in the two matrix materials.

For comparison purposes the experimentally determined γ_{PV} values for the three types of coal at 51.5°C in thymol and at 0°C in water have been corrected to 20°C. In the case of the organic matrix, thymol, the now well established surface tension temperature dependence of $\frac{d\gamma_{PV}}{dT}$ = -0.065 mJ/m²/°C was used [2]. In the case of the water/ice system a surface tension temperature dependence of $\frac{d\gamma_{PV}}{dT} = -0.14$ mJ/m²/°C, i.e. the value for water [16], was employed since the surface properties of the coal particles are apparently dominated by the adsorbed water molecules.

The data contained in Figure 3 and summarized in Table 3 indicate that in the presence of the organic matrix, thymol, the three types of coal appear to have an intermediate hydrophobicity in the range from 30-40 mJ/m^2 at 51.5°C. However, in the presence of water the three types of coal appear to be markedly more hydrophilic with surface tensions near that of water. This striking difference suggests that one and the same coal sample may have two effective surface tensions or even a range of surface tensions depending on whether the experiment is performed in organic matrix materials, e.g. thymol, or in water. These findings are in marked contrast to a similar comparison between glutaraldehyde fixed human erythrocytes, which were also studied in the same two matrix materials, i.e. thymol and water [7]. In the latter study the values of the surface tension of the cells obtained from the two matrix materials agree very well. Therefore, it appears that the present pattern of behaviour is a consequence of the heterogeneity of coal in general. Most likely, when immersed in water, the coal particles acquire a thick hydration layer so that they are perceived by the approaching water/ice solidification front as "black water particles". Such an adsorption layer is less likely in organic matrix materials. In fact, freezing front measurements with one and the same coal in different matrix materials, such as thymol, benzophenon, biphenyl and naphthalene always yielded effective surface tension values in the 30-40 mJ/m^2 range, with only small differences between matrix materials. This interpretation is further substantiated by the behaviour of coal particles of different sizes. It is well known that when coal is ground, the physical properties of the resulting coal particles often change with particle size, presumably due to the fact that variations of physical and chemical properties in a larger piece of coal influence the pattern of fracture, leading to a size dependence of physical and chemical properties, including surface properties of the particles. Such differences are indeed detected in freezing front experiments with organic matrix materials, but not with water. The fact that there is no appreciable size dependence of the surface tension of coal when measured in water is consistent with the hypothesis of an adsorbed layer of water on the coal particles.

Finally, we wish to point out that the pattern of behaviour of coal in aqueous vs. non-aqueous matrix materials is not a peculiarity or artefact of the solidification front technique, but quite general. In a subsequent paper we present results from studies of coal particle adhesion to various substrates which corroborate the results presented here [17]. Sedimentation experiments with coal powders in aqueous and non-aqueous media also produce the same type of results [18].

ACKNOWLEDGEMENTS

This work was supported by Energy, Mines and Resources, CANMET, Canada, through Contracts No. OSO82-00023 and No. OST83-00132.

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Table 1

Origin, Rank, Type of Sizing and Density of Coal Samples

COAL SAMPLE	ORIGIN	RANK AND DATE OF MINING	TYPE OF SIZING	DENSITY ρ_s (kg/m³)
B.C.	Kaiser Resources Harmer Seam Pit 29 South British Columbia	bituminous 1982	dry screened	1410
DEVCO Metallurgical	Sidney Nova Scotia	bituminous high-volatile 1982	dry screened	1370
No.3	Judy Creek Area Northern Alberta	subbituminous 1979	wet screened	1650

Table 2

Thermal & Physical Properties of Matrix Materials

Substance	Density (kg/m^3)	Viscosity ($N \cdot s/m^2$)	Specific Heat ($kJ/kg \cdot K$)	Thermal Conductivity ($J/m \cdot s \cdot K$)	Surface Tension, γ_{LV}, at Melting Point (mJ/m^2)
Thymol	925	0.00397	2.370	0.130	29.9 at 51.5°C
Biphenyl	992	0.00149	1.840	0.142	32.5 at 70°C
Benzophenon	1146	0.00515	1.856	–	39.9 at 48°C
Water	1000	0.001787	4.2177	0.561	75.6 at 0°C

Table 3

Surface Characteristics of Coal Samples from Solidification Front Experiments in Organic and Aqueous Media

	THYMOL		WATER	
Coal Sample	V_c (μm/s)	γ_{PV}[a] (mJ/m²)	V_c (μm/s)	γ_{PV}[a] (mJ/m²)
DEVCO	5.4±1.4[b]	34.4±0.7[b] (36.4)	21.7±3.2[b]	74.9±0.4[b] (72.1)
B.C.	10.3±2.4	36.6±1.0 (38.7)	34.0±2.5	74.6±0.1 (71.8)
Coal No.3	8.7±0.9	36.3±0.5 (38.4)	6.3±0.6	75.1±0.1 (72.3)

[a] The γ_{PV} values listed in parenthesis are for comparison purposes and have been corrected to 20°C (for details, see text).

[b] Mean ± Standard Deviation.

LEGENDS TO FIGURES

Figure 1

Solidification front velocity, V, as a function of particle diameter, D, for B.C. coal particles in thymol.

Figure 2

Solidification front velocity, V, as a function of particle diameter, D, for B.C. coal particles in water/ice.

Figure 3

Critical velocity, V_c, as a function of particle diameter, D, obtained from the mean of the band on plots of the type given in Figures 1 and 2. Solidification matrix as indicated:

A. B.C. Coal;

B. Devco Metallurgical;

C. Coal No.3.

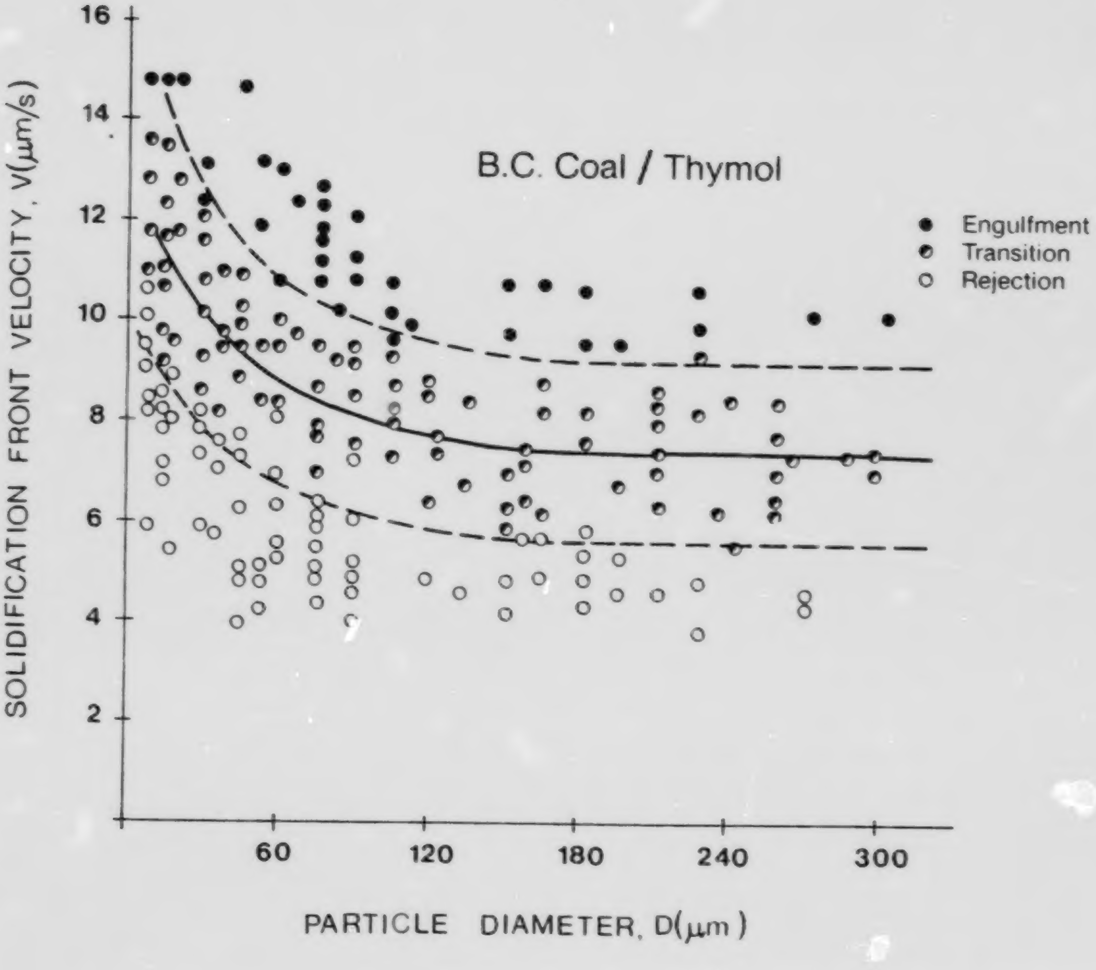
B.C. Coal / Thymol
● Engulfment
◐ Transition
○ Rejection
SOLIDIFICATION FRONT VELOCITY, V(μm/s)
PARTICLE DIAMETER, D(μm)
16
14
12
10
8
6
4
2
60
120
180
240
300

Fig. 1

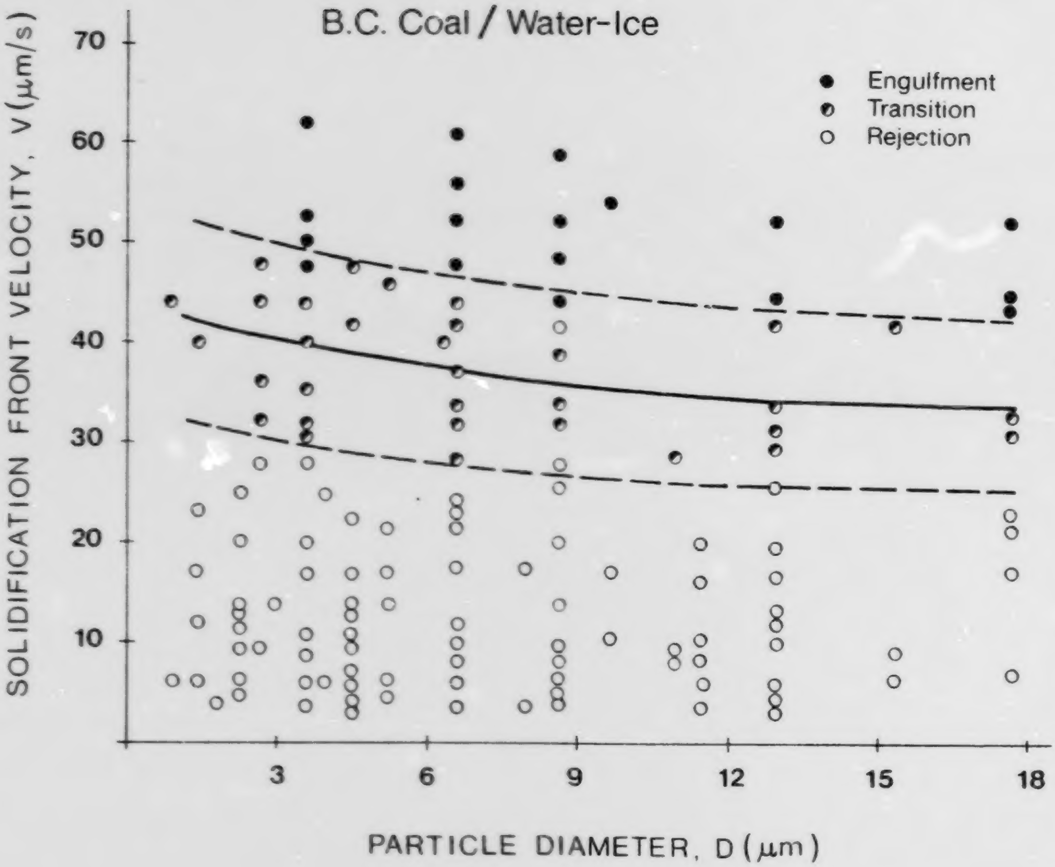
B.C. Coal / Water-Ice
● Engulfment
◐ Transition
○ Rejection
SOLIDIFICATION FRONT VELOCITY, V (μm/s)
70
60
50
40
30
20
10
3
6
9
12
15
18
PARTICLE DIAMETER, D (μm)

Fig. 2

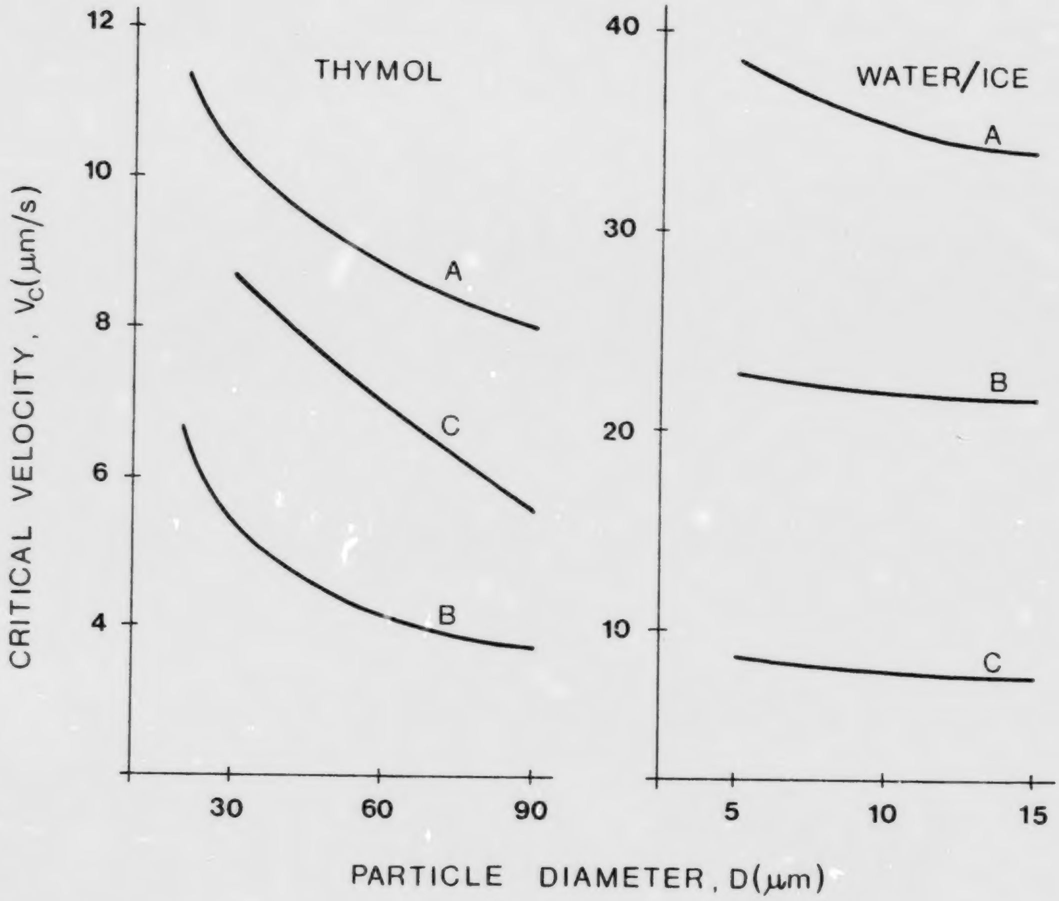
THYMOL
WATER/ICE
CRITICAL VELOCITY, V_C(μm/s)
12
10
8
6
4
40
30
20
10
A
B
C
30
60
90
5
10
15
PARTICLE DIAMETER, D(μm)

Fig. 3

KEY WORDS

Coal powder; solidification front technique; surface tension of coal; surface properties of coal powders.

STUDY No. II

SURFACE PROPERTIES OF COAL PARTICLES IN AQUEOUS MEDIA.

II. ADHESION OF COAL PARTICLES TO POLYMERIC SUBSTRATES

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ABSTRACT

The adhesion technique for the determination of the surface tension of small particles was used to characterize surface properties of three types of coal particles. It was found that in aqueous media with relatively high surface tensions the coal particles are very hydrophilic with surface tension values in the 65-70 mJ/m² range. These findings are in good agreement with data obtained from other techniques. Exploratory measurements at low surface tensions give an indication of the hydrophobic nature of coal, which normally manifests itself when suspended in organic media.

INTRODUCTION

We have previously reported on the use of the advancing solidification front technique for determining the surface tension of coal particles [1,2]. The main conclusion of that work is that coal particles appear to have two effective surface tensions, depending on the matrix material used. In the presence of a water/ice solidification matrix coal appears to be very hydrophilic and yet, when the surface tension is determined in an organic matrix, e.g. thymol, the coal particles appear to be relatively hydrophobic with surface tensions in the range of 30-40 mJ/m^2 [2]. The present work was undertaken in order to determine whether this apparent duality was peculiar to the advancing solidification front method. In order to test this possibility we here employ a strategy based on the adhesive behaviour of coal particles. This strategy has been used previously to determine the surface tension of biological particles [3-6]. In essence, the method relies on a quantitative evaluation of the extent of the interaction of coal particles with a wide range of polymer surfaces, as a function of the surface tension of various liquid mixtures, and on the interpretation of this experimental observation from a surface thermodynamic point of view.

Furthermore, since these experiments can be performed in liquid mixtures with a wide range of surface tensions, this technique enables us to test whether one and the same coal sample does in fact have two effective surface tensions depending on the properties of the suspending liquid.

THEORETICAL CONSIDERATIONS

When a natural process occurs, it will be accompanied by a change in the net free energy of the system.

In order to make a quantitative prediction we have to "model" the process under consideration. Consider a particle (P), e.g. a coal fragment, initially suspended in a liquid (L), attaching itself to a solid (S) which is also immersed in this liquid (Figure 1). In the absence of external forces as well as in the absence of any specific interactions, the change in the free energy, ΔF^{adh}, due to particle adhesion is described by

$$\Delta F^{adh} = \gamma_{PS} - \gamma_{PL} - \gamma_{SL} \quad (1)$$

where γ_{PS} and γ_{PL} are the particle-solid and particle-liquid interfacial tensions respectively, and γ_{SL} is the solid-liquid interfacial tension. The change in free energy is the maximum work obtainable from a process, here the adhesion of a particle, and the interfacial tensions are, by definition, the work required to generate the interfacial areas under consideration. (A new particle-substrate interface is created whilst the particle-liquid and substrate-liquid interfaces are partially annihilated during the process of adhesion).

The crucial point in the actual application of the thermodynamic model is the determination of values for the interfacial tensions γ_{PS}, γ_{PL} and γ_{SL} in equation (1). It is possible to obtain these data from an equation of state approach [7], which allows the calculation of the surface tension, γ_{SV}, of a solid (S) in contact with its vapour (V), from a measured liquid surface tension, γ_{LV}, and the contact angle, θ, which a drop of the liquid makes with the solid. Briefly, the technique utilizes Young's equation [8]

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \qquad (2)$$

where γ_{SV}, γ_{SL} and γ_{LV} are, respectively, the interfacial tension between a solid substrate (S) and the vapour phase (V), the interfacial tension between S and the liquid (L), and the interfacial tension between L and V; θ represents the contact angle. Of the four quantities in equation (2), only γ_{LV} and θ are readily determined experimentally; determination of a further relationship between these and the other two quantities is required. It has been shown previously, from thermodynamic considerations, that an equation of state of the form

$$\gamma_{SL} = f(\gamma_{SV}, \gamma_{LV}) \qquad (3)$$

must exist [9]. Using experimental contact angles and liquid-vapour interfacial tensions, equation (3) has been formulated explicitly [7,10]. In conjunction with experimental values for γ_{LV} and θ, γ_{SV} and γ_{SL} may thus be determined from equations (2) and (3). Considering equation (3) as a generic equation to calculate any interfacial tension, γ_{12}, from given interfacial tensions,

γ_{13} and γ_{23}, where the subscripts 1, 2 and 3 refer to different phases, all the relevant interfacial tensions in equation (1) can be computed from the surface tension of the liquid and contact angles of the solid phases involved in the process under consideration. From equation (1) we now have, using equation (3)

$$\Delta F^{adh} = \gamma_{PS} - \gamma_{PL} - \gamma_{SL} \qquad (1)$$

$$= f(\gamma_{PV},\gamma_{SV}) - f(\gamma_{PV},\gamma_{LV}) - f(\gamma_{SV},\gamma_{LV}) \qquad (4)$$

where γ_{PV}, γ_{SV} and γ_{LV} are, respectively, the particle-vapour, solid-vapour and liquid-vapour surface tensions. Thus, explicit thermodynamic predictions for the process of particle adhesion may be obtained. Computer programmes which facilitate such computations are available from the authors upon request [11]. Alternatively, tables which permit such calculations may be employed [12].

Our thermodynamic model, in conjunction with the equation of state relations, predicts patterns of behaviour considerably more complex than might be expected. As an illustration, we show in Figure 2 the calculation of the free energy of adhesion (ΔF^{adh}), for the adhesion of particles as a function of varying substrate surface tension, γ_{SV}, for the two cases where the liquid surface tension, γ_{LV}, is either smaller or larger than the surface tension of the adhering particles themselves. The input information required for such theoretical predictions is the surface tension of the adhering particle, γ_{PV}, the substrate material, γ_{SV}, and the surface tension of the suspending liquid medium, γ_{LV}.

For the case where

$$\gamma_{LV} > \gamma_{PV} \tag{5}$$

ΔF^{adh} increases with increasing γ_{SV} (increasing substrate hydrophilicity), thus predicting a decreasing extent of particle adhesion with increasing substrate surface tension, γ_{SV}, over a wide range of γ_{SV} values. On the other hand, when

$$\gamma_{LV} < \gamma_{PV} \tag{6}$$

the opposite pattern of behaviour is predicted; i.e. increasing particle adhesion with increasing γ_{SV} corresponding to a decreasing ΔF^{adh} with increasing γ_{SV}. For the limiting case where the equality

$$\gamma_{LV} = \gamma_{PV} \tag{7}$$

ΔF^{adh} becomes equal to zero independent of the value of the substrate surface tension, γ_{SV}. Thus by determining experimentally that γ_{LV} value for which particle adhesion becomes independent of substrate surface tension, γ_{SV}, the particle surface tension, γ_{PV}, can be readily obtained.

MATERIALS AND METHODS

Coal

Three coal samples have been employed in this study: DEVCO Metallurgical, B.C. Coal and Coal No.3. The coal samples were provided by EMR, CANMET, Coal Research Laboratory, Edmonton, Alberta, Canada. The origin, rank, type of sizing and density of the three coal samples are given in Table 1. Following infrasizing on a Mark II infrasizer (which is essentially an air elutriation device) the coal powders were stored under vacuum in sealed bottles protected from light at room temperature. The irregularly shaped coal particles had a size ranging from 1-20 μm. Size analysis was performed using an automatic digital image analysis system (Omnicon 3000, Bausch and Lomb, Rochester, N.Y.).

Polymers

The polymer substrates to which the coal particles adhered were prepared as described previously [13]; see Table 2. Smooth films of these polymers (except for polystyrene and sulfonated polystyrene which are already available as thin films) were made by pressing strips of the polymers between chromic acid cleaned glass microscope slides in a hydraulic heat press [14]. Immediately prior to use the films were sonicated in analytical grade ethanol and rinsed in deionized distilled water. These polymer surfaces (all substrates with the exception of sulfonated polystyrene) have no ionizable groups or semipermanent charges. They are also inert, in the sense of not containing reactive chemical groups such as hydroxyl, amine, isocyanate, etc. They thus represent a class of materials whose principal variable property is their surface tension, γ_{SV}. The surface tension of the prepared polymer surfaces (c.f. Table 2) was calculated from water contact angle data using the equation of state approach [7].

Liquids

Three liquid-liquid systems were used in this work:

(1) Dimethyl Sulfoxide/Water;

(2) Water/1-Propanol; and

(3) Thiodiethanol/1-Propanol Mixtures.

The surface tension of these mixtures was varied by employing different volume ratios of the two constituent liquids. The mixtures were chosen so as to cover a relatively wide range of liquid surface tensions which were measured by means of the Wilhelmy Balance Technique [15].

The surface tensions of the various mixtures at 23°C are listed in Table 3. Also provided, for convenience, are the approximate volume/volume compositions of each solution. It should be emphasized however that, due to evaporation, etc., these concentrations are approximate. The critical parameter is the surface tension of each mixture which, in every case, was measured immediately prior to the formation of the coal suspensions.

The coal powders at a concentration of 1 mg/mℓ of solution were mixed in Erlenmeyer flasks on a rotary shaker for 30 minutes. Thereafter 0.5 mℓ of the coal suspension was placed on the various polymer surfaces. The suspensions were retained in 60 mm diameter holes formed in teflon blocks 1 cm thick. To prevent leakage, the base of each hole was sealed with medical grade Silastic gaskets and the blocks were clamped under pressure to the polymer surface. There were three holes per block. Duplicate samples were used for each surface for each experimental condition. The top of the holes were sealed with parafilm to prevent evaporation. Thereafter the systems were incubated at room temperature for 3 days. Then the teflon blocks were removed whilst the Silastic gaskets remained, thereby leaving a thin layer of liquid over the adherent particles, thus preventing exposure to an air interface. (This step is not trivial and is necessary in order to obtain interexperiment reproducibility of the data). Thereafter the test surfaces were rinsed with water under standard conditions in order to remove non-adherent particles. Standardization of the rinsing procedure was achieved by using a Bodine motor (Bodine Electric Co., Chicago, Illinois, U.S.A.), the shaft of which was attached through a z-bar to a slide holder which moves through the rinsing medium in a horizontal direction. The motor has associated with it a speed controller. The rinsing period, velocity and path length of the rinsing motion can all be controlled and thus it is possible to rinse simultaneously all of the polymer surfaces under identical conditions and therefore to compare directly the experimental results obtained.

Following rinsing the surfaces were examined for the extent of particle adhesion per unit surface area, using an automatic computerized digital image analysis system (Omnicon 3000, Bausch and Lomb, Rochester, N.Y.) attached to a Leitz Orthoplan microscope and using a 32X long-working distance objective. The major advantage of this system is that the analysis is performed using a preprogrammed automatic stage motion control and accordingly, all operator bias and elements of subjectivity, as to which microscopic fields and how much surface area is examined, is completely removed. In this manner it is possible to quantify rapidly the extent of particle adhesion to each of the polymer surfaces under the various experimental conditions. In view of the particle size heterogeneity and since, in several instances, particles touched one another, it was decided that the extent of particle adhesion to the substrate would be quantified by simply measuring the surface area covered by the particles and expressing this as a percentage of the total polymer surface area examined. For each experimental condition the data from each of the 6 areas/polymer surface was summed in order to permit detailed statistical analysis. Which surface regions were analysed was dictated by the automatic stage motion which, since it operates in a rectilinear two-dimensional pattern, necessitated the choice of the largest square which could be fitted inside the circular area. Thus 67% of the surface area of each of the 6 areas per substrate material was examined. This rectilinear motion has the added advantage that it requires the exclusion of those areas in close proximity to the teflon walls forming the well thereby avoiding any "wall effects".

RESULTS AND DISCUSSION

Time Dependence of Adhesion

As a first step in this work the kinetics of adhesion of the various coal powders to the polymer surfaces was investigated. Typical results are shown in Figure 3. Examination of this figure reveals that the extent of particle adhesion increases rapidly and then reaches a plateau after 2 days. The extent and rate at which the maximum level of adhesion was reached varied for the individual coals and the various surfaces. However, the time at which the maximum level of adhesion was achieved occurred in all cases after approximately 2 days – thereafter no further increase was observed. Thus it was decided that all of the subsequent incubation periods would be standardized at 3 days.

The effect of the surface tension of the substrate, γ_{SV}, and of the suspending liquid, γ_{LV}, on the extent of coal particle adhesion to the various polymer surfaces is illustrated in the photomicrograph in Figure 4.

The results of the 3-day incubation experiments for the three types of coal in the 1-propanol/water mixtures are given in Figure 5. The theoretical predictions illustrated in Figure 2 and their implications are therefore substantiated experimentally. At the lowest propanol concentrations, corresponding to the highest surface tension, γ_{LV}, of the suspending liquid medium, particle adhesion decreases with increasing γ_{SV} of the substratum. As the propanol concentration is increased and the liquid surface tension, γ_{LV}, correspondingly lowered, the change in the extent of particle adhesion with increasing γ_{SV} becomes less pronounced. At a certain intermediate γ_{LV} value, specific for each type of coal, particle adhesion becomes independent of γ_{SV} and finally, at even lower values of the surface tension, γ_{LV}, adhesion increases with increasing γ_{SV}.

Two main points have to be emphasized. First, the simple thermodynamic model underlying equation (1), together with the equation of state approach for interfacial tensions [7], describes the qualitative features of coal particle adhesion, as illustrated in Figure 5, quite well. Second, the data contained in Figure 5 give rise to a novel method for determining the surface tension of the adhering particles. The thermodynamic model predicts that in the case of $\gamma_{LV} = \gamma_{PV}$ (equation (7)), ΔF^{adh} should be independent of γ_{SV}, a situation that is indeed contained in the curves of Figure 5. To investigate this concept further, the slopes of the straight lines in Figure 5 were plotted versus the liquid surface tensions, γ_{LV}, in Figure 6, by means of a second-order polynomial computer curve fit. For each of the coals investigated it is inferred that the slope becomes equal to zero at a value of γ_{LV} characteristic for each type of coal. This γ_{LV} value, according to the thermodynamic model, is equal to the surface tension, γ_{PV}, of the adhering coal particles. For example, consideration of Figure 6 reveals that for DEVCO coal the adhesion slope becomes equal to zero when γ_{LV} = 69.1 mJ/m², implying that the surface tension, γ_{PV}, of this coal is also equal to 69.1 mJ/m². These results are in reasonable agreement with the surface tension values obtained for the same coals with the advancing solidification front method [1,2] and in good agreement with sedimentation volume results [16]. The experimental results obtained with the present technique, i.e. the intercepts in Figure 6 for the three types of coal, are summarized in Table 4. Also provided, for comparison, are the surface tension data for these coals obtained via the independent method of advancing solidification front and the sedimentation volume technique.

In order to address the question as to whether the results summarized in Table 4 are influenced by the specific properties of the liquid mixtures used, we have performed similar adhesion experiments using DEVCO coal particles suspended in dimethyl sulfoxide (DMSO)/water mixtures. The results for the DEVCO coal particle surface tension (γ_{PV} = 68.6 mJ/m²) obtained using DMSO/H_2O mixtures are in good agreement with the surface tension (γ_{PV} = 69.1 mJ/m²) obtained for DEVCO coal using 1-propanol/water mixtures as the suspending liquid mixtures. Thus the thermodynamic model proposed in equation (1), and illustrated in Figure 2, can be used to describe qualitatively coal particle adhesion to a range of polymer surfaces under conditions of varying γ_{LV} and chemical composition of the suspending liquid.

We have previously investigated the surface tension of the same coal samples using the advancing solidification front technique [2]. In that work we noted that when an aqueous polar matrix material (e.g. water/ice) was used, the coal particles all appeared to be relatively hydrophilic, with surface tensions greater than 60 mJ/m². However, when non-polar organic matrix materials (e.g. thymol) were used, the same coal fractions appeared to be considerably more hydrophobic with surface tensions less than 45 mJ/m². In order to investigate this apparent dichotomy further we have used the adhesion technique to study DEVCO coal particles suspended in various 1-propanol/water mixtures with a wide range of surface tensions, γ_{LV}, as well as DEVCO coal suspended in 1-propanol/thiodiethanol mixtures, i.e. a system of relatively low surface tension, γ_{LV}.

The data for the 1-propanol/water mixtures with a wide range of surface tensions, γ_{LV}, are presented in Figure 7. The extent of DEVCO coal particle adhesion to the various polymers as a function of γ_{SV}, and the slopes of the straight lines vs. γ_{LV} are presented in Figures 7A and 7B, respectively. We note that the slope intercepts the γ_{LV} axis at γ_{LV} = 69.1 mJ/m² in agreement with the results of Figure 6B. On the other hand, focussing our attention on the two points representing the lowest values of the liquid surface tension, γ_{LV}, we note that the slope decreases with increasing surface tension, tending towards an intercept of approximately 40 mJ/m². This intercept is in general agreement with the surface tension of the coal as it manifests itself in freezing front experiments [2] as well as sedimentation experiments [16] with organic media. While the underlying thermodynamic model clearly does not cover the complexities of Figure 7, it becomes, upon reflection, clear that a material which can be hydrophilic as well as hydrophobic must exhibit features of the type shown in Figure 7. As the interpretation of Figure 7 as exhibiting a minimum near 40 mJ/m² depends crucially on a single point, near γ_{LV} = 30 mJ/m², Figure 8 presents data for the same coal in thiodiethanol/1-propanol mixtures, which also shows a minimum near 37 mJ/m², qualitatively consistent with Figure 7.

While the cause, the nature and the significance of these dual patterns of behaviour of coal are not completely understood at this time, it is important to remember that these patterns are in good qualitative agreement with the findings in the preceding paper reporting solidification front experiments with coal [2]. Furthermore, the exact pattern, i.e. a duality in the response of coal to various liquids, was also observed in sedimentation experiments [16].

CONCLUSIONS

1. The experimentally observed pattern and extent of coal particle adhesion to polymeric substrata, from aqueous media, can be predicted to a considerable extent by the thermodynamic model. The observed pattern of coal

particle adhesion is similar to that reported previously for biological particle adhesion, suggesting that these thermodynamic patterns of behaviour are quite general.
2. The determination of the extent of coal particle adhesion to polymeric substrates provides a method for the determination of the surface tension of the various coal specimens. The coal studied here were all found to be relatively hydrophilic, with surface tensions in the range of the mid- to high-60's (mJ/m^2) in high energy liquids, and comparatively hydrophobic when measured in low energy liquids. The surface tension values obtained from coal adhesion studies are in good qualitative agreement with the values obtained from the advancing solidification front method [2] as well as those obtained from sedimentation volume studies [16]. The significance of coal having two apparent surface tensions is as yet not completely understood. However, it is unlikely that this pattern of behaviour is restricted to coal.

ACKNOWLEDGEMENTS

This work was supported by Energy, Mines and Resources, CANMET, Canada, through contract No. OST83-00132.

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Table 1

Origin, Rank, Type of Sizing and Density of Coal Samples

COAL SAMPLE	ORIGIN	RANK AND DATE OF MINING	TYPE OF SIZING	DENSITY ρ_s (kg/m³)
B.C.	Kaiser Resources Harmer Seam Pit 29 South British Columbia	bituminous 1982	dry screened	1410
DEVCO Metallurgical	Sidney Nova Scotia	bituminous high-volatile 1982	dry screened	1370
No.3	Judy Creek Area Northern Alberta	subbituminous 1979	wet screened	1650

Table 2

Solid Substrates Used in the Coal Adhesion Experiments

MATERIAL	SOURCE	PREPARATION	CONTACT ANGLE H_2O	SURFACE TENSION γ_{SV}, erg/cm²
Fluorinated Ethylene-propylene Copolymer (FEP)	Commercial Plastics Toronto, Canada	Heat Press	110 ± 3	16.4
Polystyrene (PS)	Central Research Lab. Dow Chemical Co.	Film	95 ± 2	25.6
Low Density Polyethylene (LDPE)	Commercial Plastica Toronto, Canada	Heat Press	84 ± 4	32.5
Polyethyleneterephtalate (PET)	Hoechst Canada Inc. Willowdale, Ontario	Film	60 ± 2	47.0
Sulfonated Polystyrene (SPS)	Central Research Lab. Dow Chemical Co.	Film	24 ± 3	66.7

Table 3

Suspending Liquid Mixtures for the Coal Adhesion Experiments

MEDIUM		APPROXIMATE CONCENTRATIONS[a]	SURFACE TENSION[a] γ_{LV} (mJ/m²)
H_2O			72.8
H_2O/1-Propanol	0.1	0.1% (vol/vol) 1-Propanol	71.3
"	0.2	0.2% (v/v)	70.2
"	0.5	0.5% (v/v)	67.3
"	1.0	1.0% (v/v)	64.0
"	2.5	2.5% (v/v)	56.0
"	5.0	5.0% (v/v)	49.0
"	10.0	10.0% (v/v)	37.8
"	20.0	20.0% (v/v)	29.1
H_2O/DMSO	1	1% (vol/vol) DMSO[b]	70.4
"	3	3% (v/v)	69.5
"	5	5% (v/v)	68.1
"	8	8% (v/v)	64.5
"	10	10% (v/v)	61.9
"	15	15% (v/v)	61.3
Thiodiethanol/1-Propanol	10	10.0% (vol/vol) 1-Propanol	43.2
"	15	15.0% (v/v)	40.0
"	20	20.0% (v/v)	37.6
"	22.5	22.5% (v/v)	36.7
"	25.0	25.0% (v/v)	35.1
"	30.0	30.0% (v/v)	34.0
"	40.0	40.0% (v/v)	31.4
"	50.0	50.0% (v/v)	29.7

[a] Since these liquids are quite hygroscopic the apparent concentrations fluctuate considerably as a function of the time the bottle has been opened; the critical value is the surface tension, (γ_{LV}), measured immediately prior to use.

[b] Dimethyl sulfoxide (Fisher Scientific)

Table 4

Particle Surface Tension, γ_{SV}, of Coal Fractions Below 400 Mesh Obtained from the Solidification Front, Sedimentation Volume and Adhesion Techniques in Aqueous Media

COAL SAMPLE -400 Mesh	PARTICLE SURFACE TENSION, γ_{SV}, (mJ/m^2), AT 20°C OBTAINED FROM			
	SOLIDIFICATION FRONT IN Water/Ice	SEDIMENTATION VOLUME IN DMSO/Water	ADHESION IN DMSO/Water	ADHESION IN 1-Propanol/Water
B.C.	71.8	70.9	-	69.0
DEVCO	72.1	69.0	68.6	69.1
No.3	72.3	64.4	-	64.9

LEGENDS TO FIGURES

Figure 1

Schematic Representation of the Process of Particle Adhesion. P: Particle; L: Suspending Liquid; S: Polymer Substrate.

Figure 2

The Free Energy of Adhesion, ΔF^{adh}, for Coal Particles as a Function of Substrate Surface Tension, γ_{SV}:

A. $\gamma_{LV} > \gamma_{PV}$;

B. $\gamma_{LV} < \gamma_{PV}$.

Figure 3

Adsorption Isotherm of DEVCO Coal Particles Suspended in a Mixture of Thiodiethanol and 1-Propanol (γ_{LV} = 40.0 mJ/m²) as a Function of Time. Substrate is Polyethyleneterephthalate, γ_{SV} = 47.0 mJ/m².

Figure 4

Photomicrographs of DEVCO Coal Particle Adhesion Under Varying Conditions:

(a) Fluorinated Ethylene Propylene

(FEP: γ_{SV} = 16.4 mJ/m²); γ_{LV} = 72.5 mJ/m²;

(b) Sulfonated Polystyrene

(SPS: γ_{SV} = 66.7 mJ/m²); γ_{LV} = 72.5 mJ/m²;

(c) Fluorinated Ethylene Propylene

(FEP: γ_{SV} = 16.4 mJ/m²); γ_{LV} = 56.1 mJ/m²;

(d) Sulfonated Polystyrene

(SPS: γ_{SV} = 66.7 mJ/m^2); γ_{LV} = 56.1 mJ/m^2. Suspending Liquid Mixtures are Formed from Various Concentrations of 1-Propanol and Water.

Figure 5

Extent of Coal Particle Adhesion as a Function of Substrate Surface Tension, γ_{SV}, for Various 1-Propanol/H_2O concentrations:

A. B.C. Coal;

B. DEVCO Metallurgical Coal;

C. Coal No.3.

Figure 6

Slopes of the Straight Lines of Figure 6 versus γ_{LV}:

A. B.C. Coal;

B. DEVCO Metallurgical Coal;

C. Coal No.3.

The Slope is Equal to Zero for $\gamma_{LV} = \gamma_{PV}$.

Figure 7

DEVCO Coal Particle Adhesion to Polymer Surfaces when Suspended in 1-Propanol/Water Mixtures with Low Surface Tensions:

A. Extent of Particle Adhesion as a Function of Substrate Surface Tension, γ_{SV}, for Various γ_{LV} Values.

B. Slope of the Straight Lines versus γ_{LV}.

Figure 8

Slopes of the Straight Lines *versus* γ_{LV} for Various Thiodiethanol/1-Propanol Mixtures. Coal Sample is DEVCO Metallurgical and Substrates as Indicated in Table 2.

$$\Delta F^{adh} = \gamma_{PS} - \gamma_{SL} - \gamma_{PL}$$

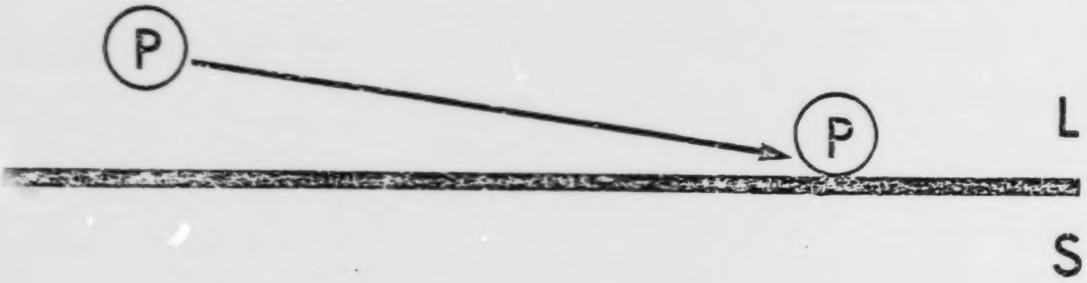

Fig. 1

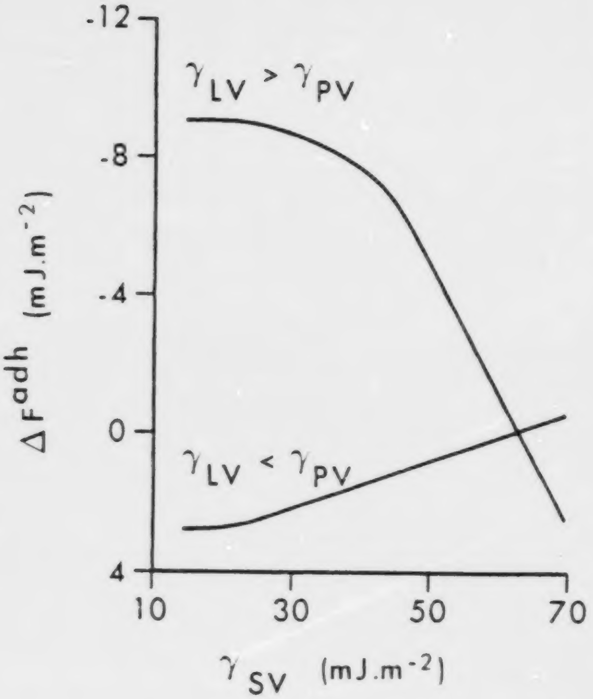
-12
-8
-4
0
4
10
30
50
70
ΔF^{adh} (mJ.m^{-2})
γ_{SV} (mJ.m^{-2})
$\gamma_{LV} > \gamma_{PV}$
$\gamma_{LV} < \gamma_{PV}$

Fig. 2

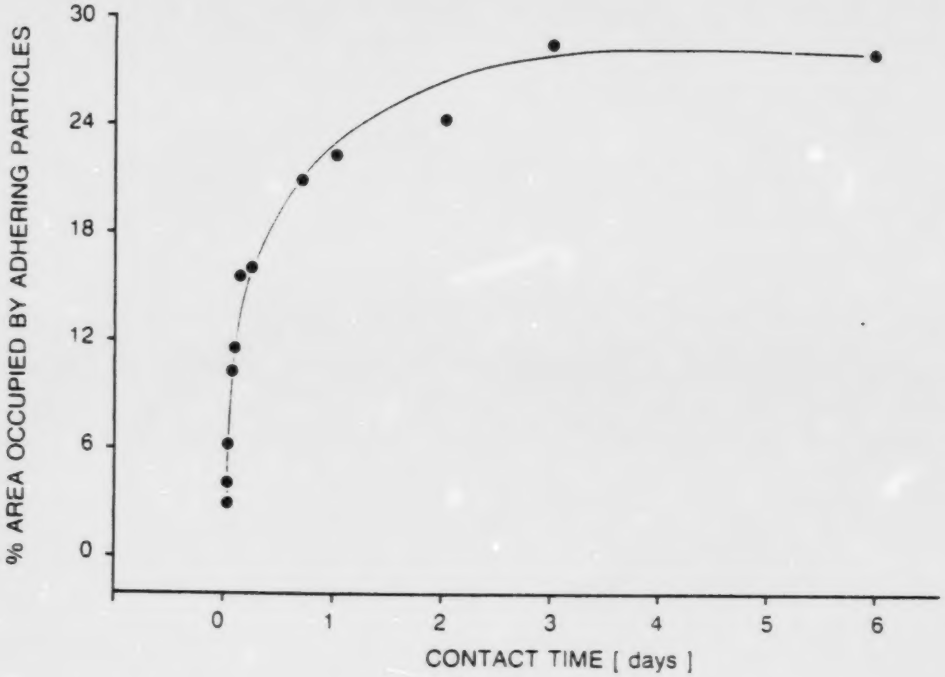
% AREA OCCUPIED BY ADHERING PARTICLES
30
24
18
12
6
0
0
1
2
3
4
5
6
CONTACT TIME [days]

Fig. 3

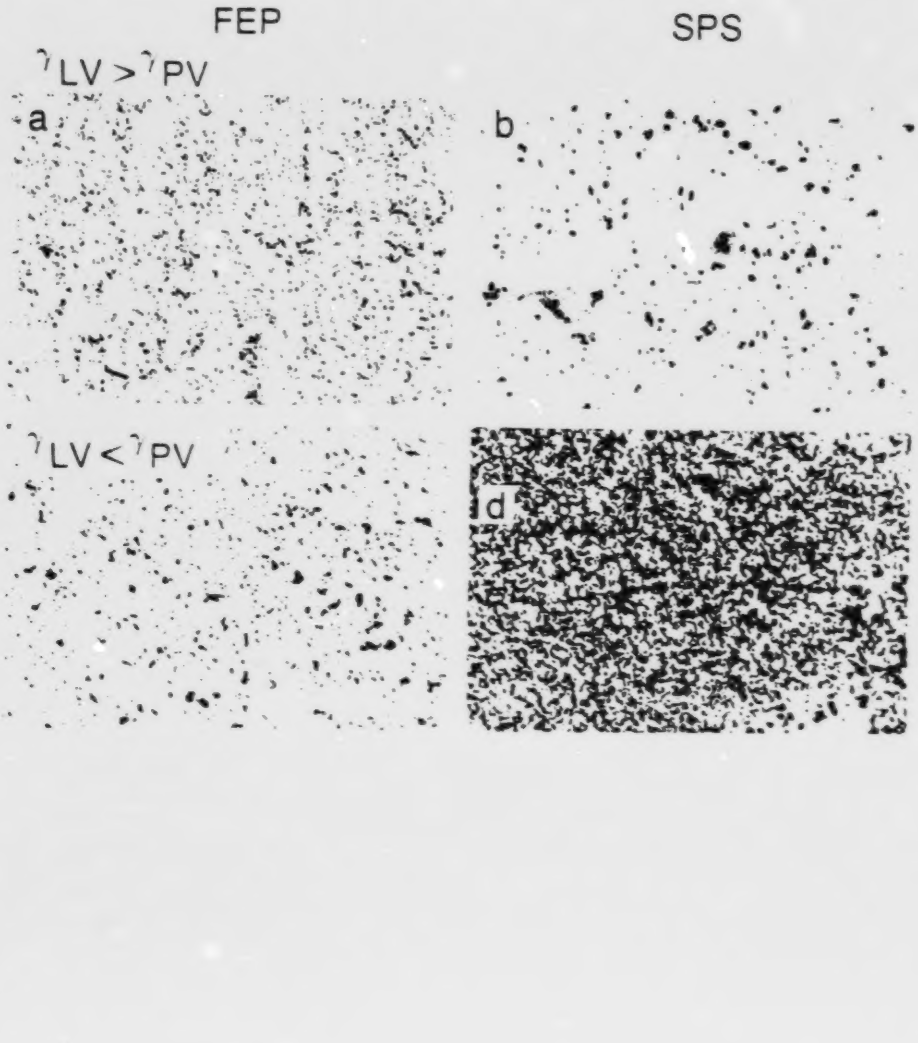
FEP
SPS
γLV > γPV
a
b
γLV < γPV
d

Fig. 4

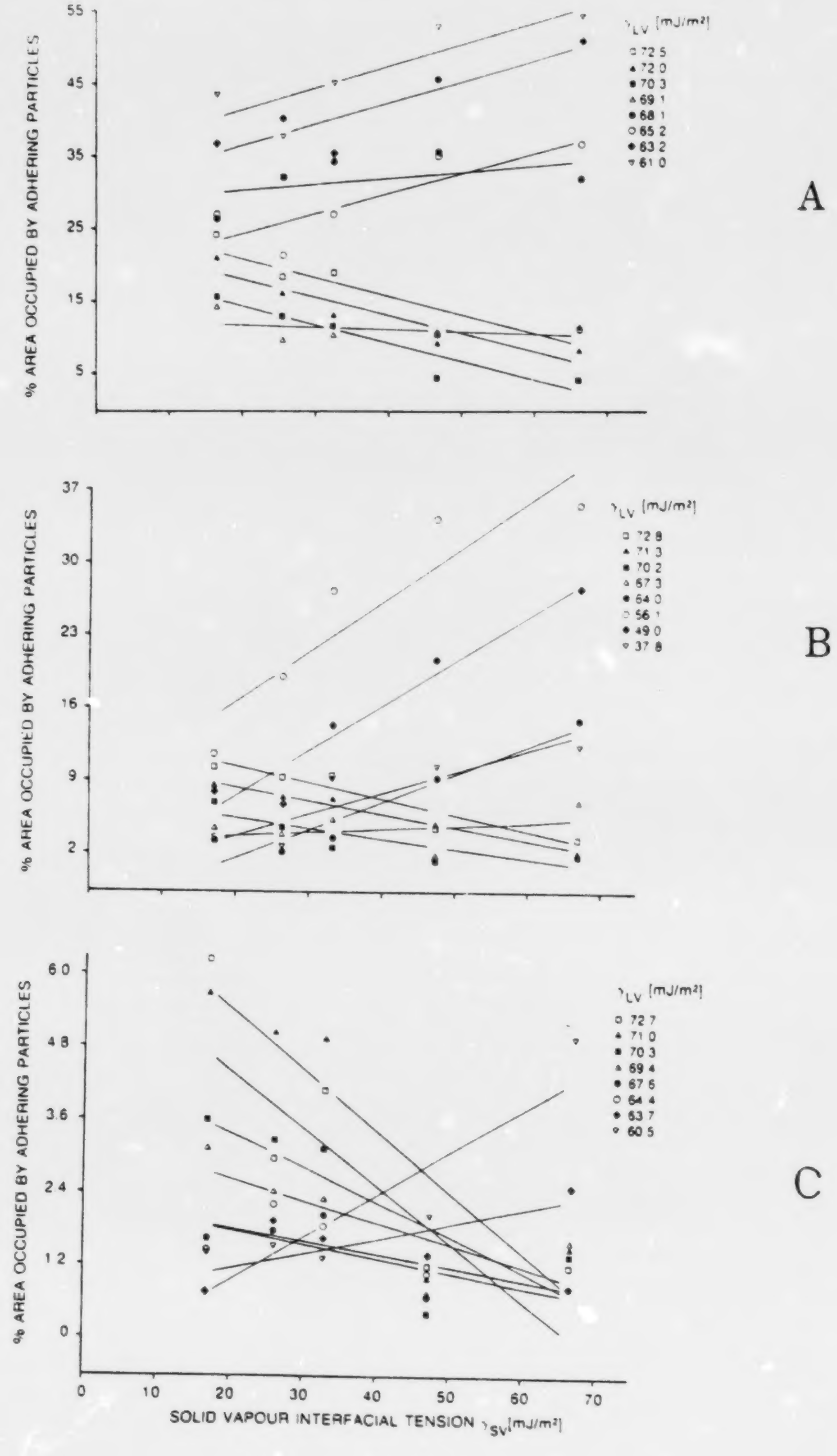
55
45
35
25
15
5
% AREA OCCUPIED BY ADHERING PARTICLES
γ_{LV} [mJ/m²]
72.5
72.0
70.3
69.1
68.1
65.2
63.2
61.0
A
37
30
23
16
9
2
% AREA OCCUPIED BY ADHERING PARTICLES
γ_{LV} [mJ/m²]
72.8
71.3
70.2
67.3
64.0
56.1
49.0
37.8
B
6.0
4.8
3.6
2.4
1.2
0
% AREA OCCUPIED BY ADHERING PARTICLES
γ_{LV} [mJ/m²]
72.7
71.0
70.3
69.4
67.6
64.4
63.7
60.5
C
0
10
20
30
40
50
60
70
SOLID VAPOUR INTERFACIAL TENSION γ_{SV} [mJ/m²]

Fig. 5

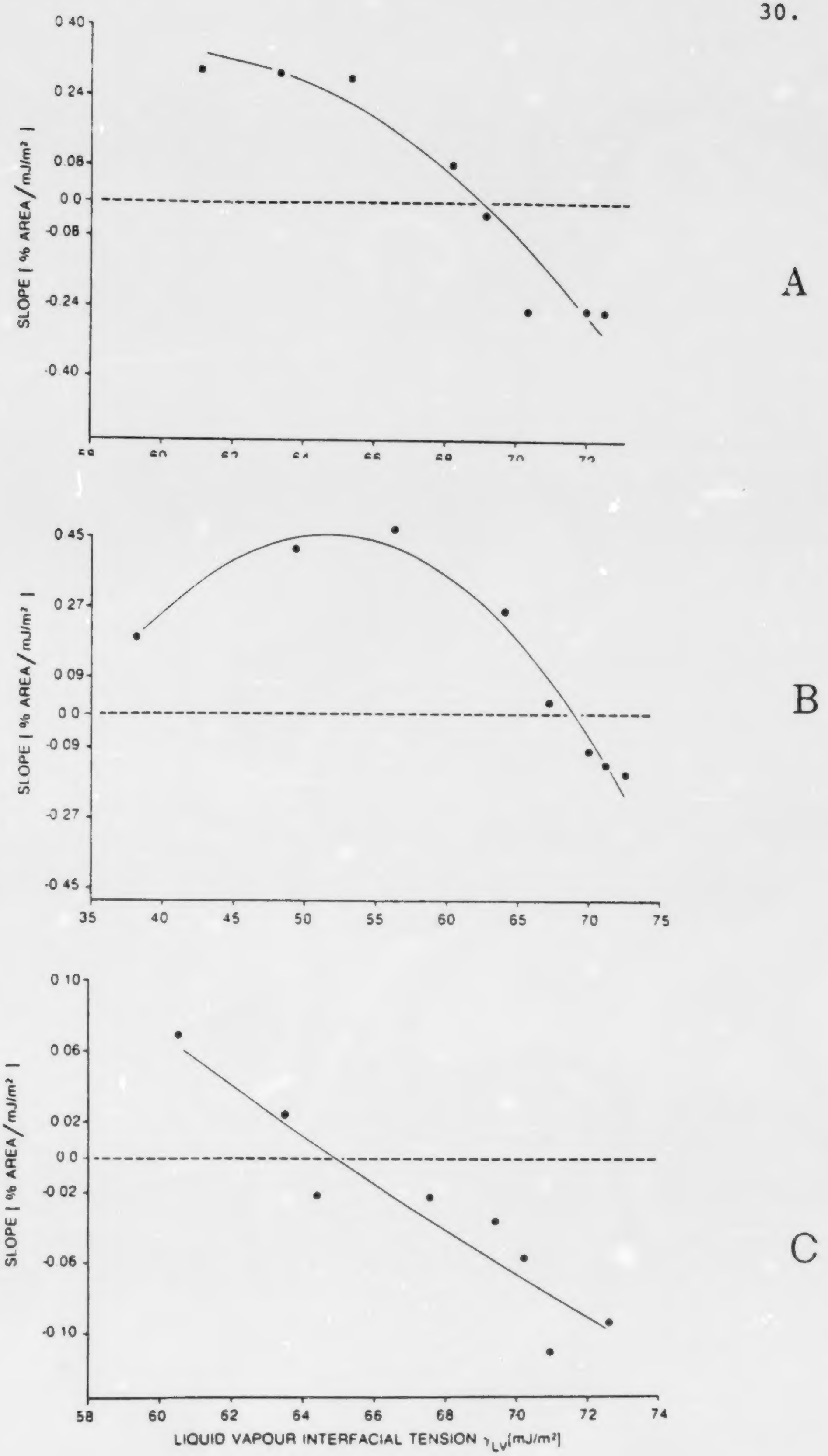
0.40
0.24
0.08
0.0
-0.08
-0.24
-0.40
SLOPE [% AREA/mJ/m²]
A
0.45
0.27
0.09
0.0
-0.09
-0.27
-0.45
35
40
45
50
55
60
65
70
75
B
0.10
0.06
0.02
0.0
-0.02
-0.06
-0.10
58
60
62
64
66
68
70
72
74
C
LIQUID VAPOUR INTERFACIAL TENSION γ_{LV} [mJ/m²]

Fig. 6

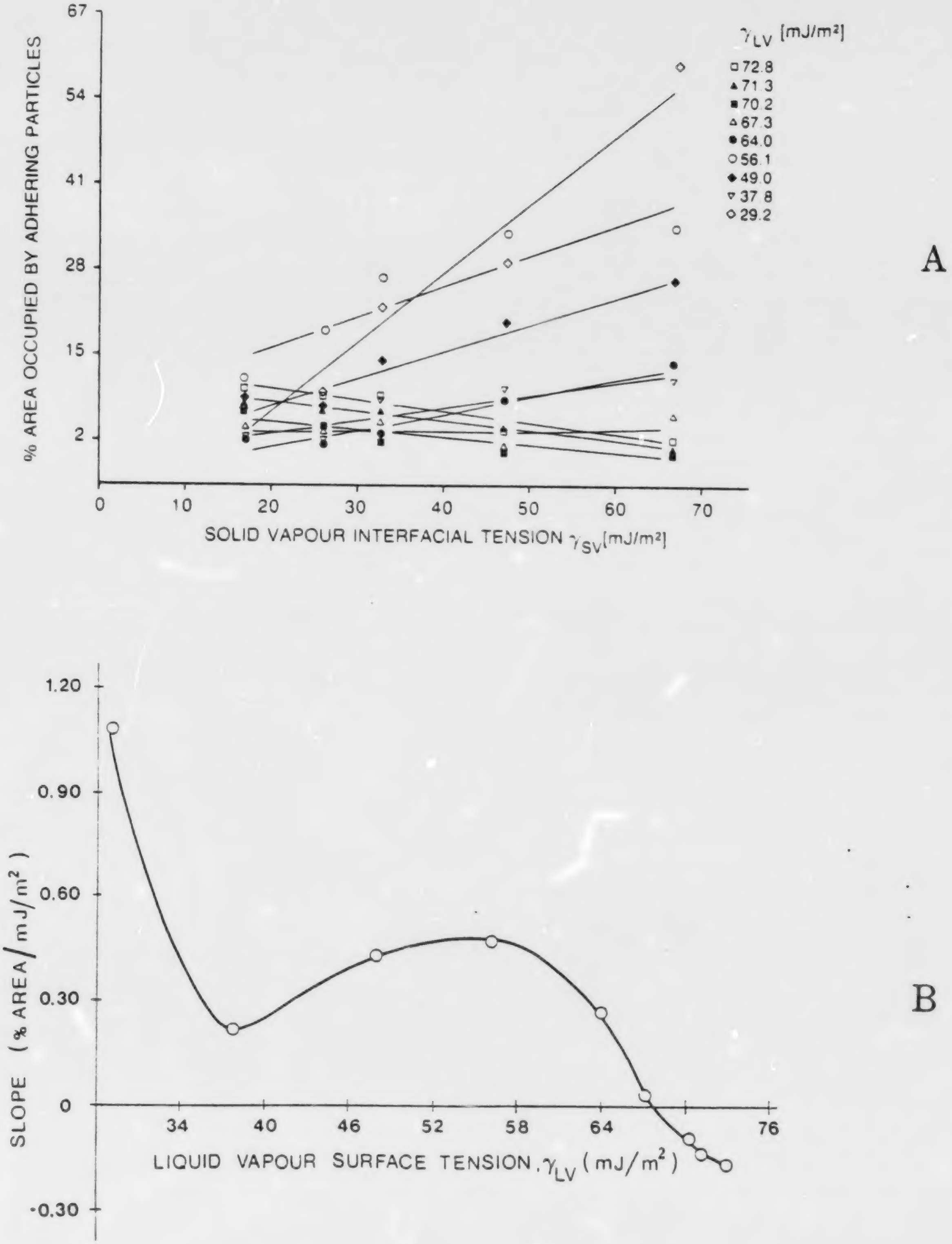
67
54
41
28
15
2
% AREA OCCUPIED BY ADHERING PARTICLES
0
10
20
30
40
50
60
70
SOLID VAPOUR INTERFACIAL TENSION γ_{SV} [mJ/m²]
γ_{LV} [mJ/m²]
□ 72.8
▲ 71.3
■ 70.2
△ 67.3
● 64.0
○ 56.1
◆ 49.0
▽ 37.8
◇ 29.2
A
1.20
0.90
0.60
0.30
0
-0.30
SLOPE (% AREA/mJ/m²)
34
40
46
52
58
64
76
LIQUID VAPOUR SURFACE TENSION, γ_{LV} (mJ/m²)
B

Fig. 7

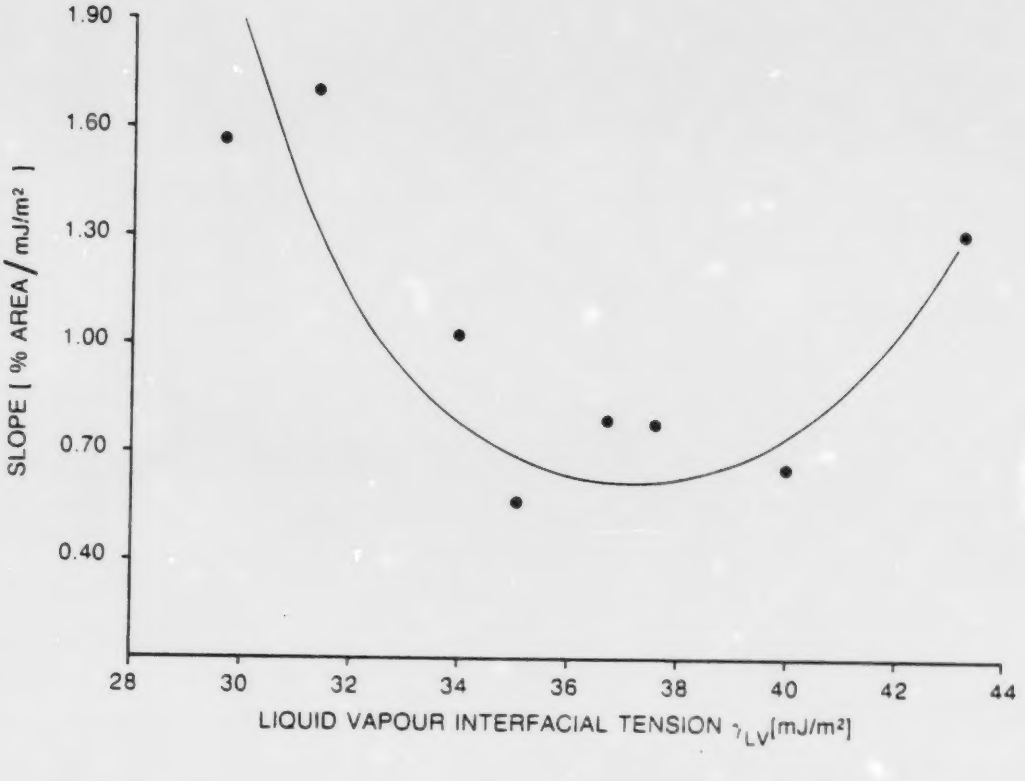
1.90
1.60
1.30
1.00
0.70
0.40
SLOPE [% AREA / mJ/m²]
28
30
32
34
36
38
40
42
44
LIQUID VAPOUR INTERFACIAL TENSION γ_{LV}[mJ/m²]

Fig. 8

KEY WORDS

Coal powder; adhesion technique; surface tension of coal; wettability of coal particles.

STUDY No. III

SURFACE TENSION EFFECTS IN THE SEDIMENTATION OF POLYMER PARTICLES IN VARIOUS LIQUID MIXTURES

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ABSTRACT

The sedimentation volume, V_{sed}, of polymer particles in mixtures of pairs of nonpolar as well as polar liquid combinations was determined at 20°C.

The liquid combinations were chosen such that the interfacial tension, γ_{SV}, of the polymer particles fell between the surface tensions of the two liquids. Constant amounts of a given polymer powder were suspended in constant volumes of liquid mixtures of different concentrations.

It was found that the sedimentation volume changed with the composition and hence the surface tension of the liquid mixtures. A maximum or a minimum occurred in V_{sed} when the surface tension of the suspending liquid was equal to that of the particles, i.e., when $\gamma_{LV} = \gamma_{SV}$. Maxima occurred in the polar and minima in the nonpolar and slightly polar liquid mixtures.

The results are discussed in terms of van der Waals interactions and mechanisms of particle aggregation.

INTRODUCTION

Sedimentation experiments are a well established technique to study the stability of dispersions of powders in liquids. While in many cases the behaviour of such systems is believed to be governed by van der Waals and electrostatic interactions, it is to be expected that for polymer particles, particularly in non-aqueous media, the effect of the electrostatic interactions may be considered negligible in comparison with the van der Waals interactions. It was found in recent years[1] that there is a strong correlation between van der Waals type interactions and surface tensions. The van der Waals interaction between two parallel, infinitely extended flat surfaces in a liquid medium was first calculated by Hamaker.[2] For the work done in bringing these surfaces from infinity to a distance d_0 he obtained

$$W = -\frac{A_{132}}{12\pi d_0^2} \qquad (1)$$

where the coefficient A_{132} has subsequently been called "Hamaker coefficient". If we assume that d_0 is so small that we in fact have contact between the two solid phases, this work is the thermodynamic free energy of adhesion

$$\Delta F^{adh} = \gamma_{12} - \gamma_{13} - \gamma_{23} \qquad (2)$$

where γ denotes interfacial tensions and the indices 1, 2 and 3 refer, respectively, to solid (1), solid (2) and liquid (3).

It has been shown that the free energy of adhesion can be positive, negative or zero, implying that van der Waals interactions can be attractive as well as repulsive.[1,3,4] While equation (1) can, strictly speaking, be expected to hold only for systems which interact by means of dispersion forces only, there are no such restrictions on equation (2). Since equation (2) describes fundamental patterns of the behaviour of particles including macromolecules[5] very well, independent of the type of molecular interactions present, we found it convenient to define an "effective Hamaker coefficient" which reflects the free energy of adhesion.[1]

While van der Waals interactions between unlike solids in a liquid may be attractive as well as repulsive, it is clear from the underlying thermodynamics[3,6] that like particles can only attract each other, with zero interaction in the limiting case where the surface tension of the suspending liquid, γ_{LV}, is equal to the particle surface tension, γ_{SV}. Thus it becomes a matter of interest to perform sedimentation experiments with polymer particles of known surface tension, in liquids of lower, equal and higher surface tension than the polymer. It is the purpose of this paper to present initial results of experiments performed under these guidelines. In order to be able to control and vary the surface tension of the suspending liquids, binary mixtures were chosen of pairs of liquids such that one had a lower and the other a higher surface tension than the polymer particles.

It is interesting to speculate on what might happen to the sedimentation volume in the special case when $\gamma_{LV} = \gamma_{SV}$. There are at least two possible patterns of behaviour, depending on whether or not agglomeration of the particles at the early stages of sedimentation is possible.

a) If there is no agglomeration at finite values of the van der Waals attraction, then for zero van der Waals attraction least close packing of the sediment and hence a maximum of V_{sed} is expected.

b) If there is agglomeration at finite values of the van der Waals attraction at early stages of sedimentation, then this agglomeration would cease when the van der Waals attraction approaches zero. Since the irregularly shaped aggregates resulting from agglomeration do not pack well, one would expect minimum sedimentation volume at zero van der Waals attraction.

Clearly, we have here two possible mechanisms for the formation of the final sediment, one predicting a minimum and the other a maximum of the sedimentation volume when $\gamma_{LV} = \gamma_{SV}$. It was anticipated that simple sedimentation experiments would not only test the expectation of a correlation between sedimentation volume and particle as well as liquid surface tension, but also shed light on the question of mechanisms of particle interaction.

In order to determine the surface tension, γ_{SV}, of the various polymers used in the sedimentation experiments contact angles were measured on films of polymers prepared either by heat pressing or solvent casting. The surface tensions, γ_{SV}, were calculated by means of an equation of state approach.[6]

EXPERIMENTAL

1. MATERIALS

1.1 Polymers

The sedimentation experiments were performed with the following polymer powders: (1) Polytetrafluoroethylene (Teflon), PTFE; two samples with different particle size were used: Grade 1 (Polysciences Inc.) and No. 6 (duPont); (2) Polyvinylidenefluoride, PVDF (Polysciences Inc.); (3) Polyvinylfluoride, PVF (Polysciences Inc.); (4) High density polyethylene, HDPE (duPont); (5) Polyhexamethylene adipamide (Nylon 66), PA 66, (Commercial Plastics); (6) Polysulfone, PSF (Union Carbide Corp.).

Polymer films of PTFE, PVDF, HDPE and PSF were prepared by heat pressing, while the films of PVF and PA 66 were prepared by solvent casting.[7] The polymer films were used for contact angle measurements with water to determine the solid/vapour surface tension, γ_{SV}, of the polymers.

The density,[8,9] ρ, surface tension, γ_{SV}, and the particle size range (determined by light microscopy) of the polymers are summarized in Table 1.

TABLE 1

Physical Properties of Polymers

Polymer		Density ρ (kg/m^3)	Ref.	Surface Tension γ_{SV} (mJ/m^2)	Particle Size Range D (μm)
Polytetrafluoro ethylene PTFE	Grade 1	2000	8	20.0	500-600
	No. 6				200-400
Polyvinylidenefluoride PVDF		1740	9	25.5	3-30
Polyvinylfluoride PVF		1380	9	29.4	2-35
Polyethylene HDPE	high density	965	8	30.3	30-120
Polyhexamethylene adipamide, Nylon 66 PA 66		1090	8	41.1	60-250
Polysulfone PSF		1240	9	43.1	10-100

1.2 Organic Liquids

The sedimentation volume, V_{sed}, of the polymer powders was determined in mixtures of pairs of nonpolar as well as polar liquid combinations. The liquid combinations were chosen such that the surface tension, γ_{L_1V}, of one liquid was lower and that of the second one, γ_{L_2V}, was higher than that of the polymer particles, γ_{SV}.

There are several conditions which the suspending liquids must satisfy in order to be used for the sedimentation experiments. The criteria for choosing the liquid components are: (1) they should be chemically inert with respect to the solid particles; (2) the boiling temperature should be reasonably high to minimize evaporation; (3) the density of the liquids should be lower than that of the particles; (4) liquids with zero or nearly zero dipole moment as well as with higher dipole moment should be found to cover a wide polarity range; (5) the liquid components should be miscible in all ratios with each other; and (6) the surface tension, γ_{LV}, of the liquid mixtures should cover the surface tension range required.

The liquids selected according to those criteria together with their relevant boiling points,[10,11] density,[10] dipole moment[9,10,12] and surface tension[12,13] are presented in Table 2.

2. METHODS

2.1 Surface Tension of Polymers from Contact Angle Measurements

In order to establish the solid/vapour interfacial tension, γ_{SV}, of those polymers for which this information was not available (PVDF, PVF, HDPE and PSF), contact angles, Θ, of water was measured on the smooth surfaces of polymers (prepared from the polymer powders used for sedimentation) by the sessile drop method. The surface tension, γ_{SV}, of polymers was then calculated by using our equation of state relation.[6,14] (see Tables 1 and 5).

TABLE 2

Physical Properties of Liquids Used for Sedimentation

Liquids		Boiling Point b.p. (^{o}C)	Density at $20^{o}C$ ρ_L (kg/m^3)	Dipole Moment at $20^{o}C$ $\mu x 10^{-30}$ (Cm)	Surface Tension at $20^{o}C$ γ_{LV} (mJ/m^2)	
					Literature	Measured
n-Hexane	C_6H_{14}	68.95	660.3	0	18.40	18.3
n-Octane	C_8H_{18}	125.66	702.5	0	21.62	21.8
n-Hexadecane	$C_{16}H_{34}$	286.80	773.3	0	27.47	27.0
Tetralin	$C_{10}H_{12}$	207.57	970.2	1.63	35.60	36.5
Diethyl ether	$C_4H_{10}O$	34.51	713.8	3.84	17.10	17.4
n-Propanol	C_3H_8O	97.40	803.5	5.60	23.71	23.8
n-Hexanol	$C_6H_{14}O$	157.85	813.6	5.17	26.21	25.2
Ethylene glycol	$C_2H_6O_2$	198.93	1108.8	7.61	48.43	48.9
Cyclohexanone	$C_6H_{10}O$	155.65	947.8	9.01	35.19	34.3
2,2' Thiodiethanol	$C_4H_{10}O_2S$	117^{733}	994.0	not available	54.00	52.5

2.2 Preparation of Liquid Mixtures

For the sedimentation experiments, the following seven pairs of liquids were chosen from the ten liquids in Table 2:

(1) n-hexane/n-hexadecane,
(2) n-octane/tetralin (1,2,3,4 tetrahydronaphtalene),
(3) diethyl ether/tetralin,
(4) diethyl ether/n-hexanol,
(5) diethyl ether/ethylene glycol (1,2 ethanediol),
(6) n-propanol/cyclohexanone, and
(7) n-propanol/2,2' thiodiethenol

These liquids were Aldrich, Baker and/or Fluka reagents (certified laboratory grade).

The liquid/vapour surface tension, γ_{LV}, of the different liquid compositions as well as that of the pure solvents was determined (for the pure components, see Table 2) by means of the modified Wilhelmy method at $20^{\circ}C$ prior to the sedimentation measurements.

2.3 Determination of the Sedimentation Volume, V_{sed}

Prior to the actual sedimentation experiments, the polymer powders were thoroughly agitated in the appropriate liquids in order to break up any aggregates and to displace air bubbles. For this purpose, constant amounts of a given polymer powder were weighed into small polyethylene micro centrifuge tubes with well fitting lids. The amount of polymer powder used varied from 0.05 to 0.20 grams depending on the density and/or the particle size of the powder. To be specific, 0.20 g was weighed in for both PTFE samples, 0.05 g for PVF, and 0.10 g for all other polymers. The powder was weighed with analytical accuracy. The powders in the centrifuge tubes were then suspended with approximately 0.1 to 0.2 ml liquids with different compositions by agitating the samples for at least five minutes using a test tube mixer. In order to achieve complete displacement of air, the samples were left at least for two hours and then agitated again for another five minutes.

For the actual sedimentation experiments, graduated micro test tubes (100 mm high with an inner diameter of 3 mm) were used. The total volume, 1.00 ml, of these tubes is divided into 100 graduations, and the sedimentation volume was read (or estimated) to 0.1 of a graduation, i.e. to 0.001 ml.

Each of the dispersions prepared in the centrifuge tubes was then transferred into a microtube using Pasteur micropipettes. The selected liquid mixture was used as rinsing liquid in each case. Finally, the microtubes were filled up to 1.00 ml with the liquid mixture. Then the microtubes were sealed and shaken for approximately five minutes so that the polymer powder was totally and homogeneously suspended in the liquid medium. The reading of the sedimentation volume, V_{sed}, of the polymer powder was taken every day for three days to one week, depending on the sample, until no further change in V_{sed} occurred.

RESULTS AND DISCUSSION

Photographs on the sedimentation volume of PTFE (Grade 1) powder suspended in liquid pairs of n-hexane/n-hexadecane and of diethyl ether/n-hexanol are shown in Figures 1 and 2, respectively. These sedimentation volumes, V_{sed}, are plotted in Figure 3 as a function of the surface tension, γ_{LV}, of the suspending liquids. Data for an additional system, i.e. diethyl ether/tetralin are also given in Figure 3. Since these experiments are time consuming, reproducibility testing was limited to performing two independent experiments for one and the same system, Teflon/n-hexane/n-hexadecane, as shown in Figure 4. While the two curves do not coincide, they show the common relevant feature, i.e. a minimum at $\gamma_{LV} = 20.0$ mJ/m^2 in each case. The sedimentation volume as a function of the surface tension of the suspending liquids are given in Figures 5 to 10 for the other six polymers investigated in various liquid combinations.

It is apparent that the final sedimentation volume, V_{sed}, changes with composition and hence surface tension, γ_{LV}, of the liquid mixtures such that it shows an extremum at a certain liquid surface tension. It turns out that these extrema are minima in the case of nonpolar and slightly polar liquid combinations such as n-hexane/n-hexadecane, or diethyl ether/tetralin. In the case of more polar liquids, such as mixtures of diethyl ether/n-hexanol and n-propanol/ethylene glycol the extrema are maxima. The types of extremum of the sedimentation volume, V_{sed}, obtained for the seven polymers in the various liquid combinations are given in Table 3 together with the surface tension and dipole moment range of the liquid pairs.

The surface tensions, γ_{LV}, of the liquid mixtures at which the extrema occur are summarized in Table 4 for the various polymers. For each polymer, the average value is given in Table 5. The contact angles with water, obtained for the various polymers and the polymer surface tension, γ_{SV}, calculated from the contact angles are also listed in Table 5. The agreement between these data and those corresponding to the sedimentation volume extrema is so striking that it seems justified to suggest that the sedimentation technique might be considered a means to determine the surface tension of solids in powder form, or for that matter, for any small particles, including biological cells.

The result that we have maxima in some cases and minima in others might suggest that both of the possible mechanisms described in the introduction are operative. This suggestion is further corroborated by the fact that it is far easier to resuspend the systems where we had observed maxima, than those where we had minima. This observation is in keeping with the hypothesis of a correspondence between absence of aggregation

TABLE 3

Type of Extremum of Sedimentation Volume, V_{sed}, for the Polymers Investigated in Liquids of Different Polarity

Liquid Pairs Used for Sedimentation	Surface Tension Range γ_{LV} (mJ/m^2)	Dipole Moment Range $\mu x10^{-30}$ (Cm)	Type of V_{sed} Extremum Obtained for					
			PTFE	PVDF	PVF	HDPE	PA 66	PSF
n-Hexane n-Hexadecane	18.3 27.0	0 0	min					
n-Octane Tetralin	21.8 36.5	0 1.63		min	min	min		
Diethyl ether Tetralin	17.4 36.5	3.84 1.63	min			min		
Diethyl ether n-Hexanol	17.4 25.2	3.84 5.17	max					
n-Propanol Ethylene glycol	23.8 48.9	5.60 7.61		max	max		max	max
n-Propanol Cyclohexanone	23.8 34.3	5.60 9.01				max		
n-Propanol Thiodiethanol	23.8 52.5	5.60 ?					max	max

TABLE 4

Extrema of Sedimentation Volumes for Polymers in Different Liquid Combinations

Polymers / Liquid Combinations	V_{sed} Extremum at γ_{LV} of Liquids at 20°C (mJ/m^2)						
	PTFE		PVDF	PVF	HDPE	PA 66	PSF
	Grade 1	No.6					
n-Hexane n-Hexadecane	20.0	20.0					
n-Octane Tetralin			27.1	29.0	29.2		
Diethyl ether Tetralin	20.1	19.6			28.4		
Diethyl ether n-Hexanol	20.2	19.4					
n-Propanol Ethylene glycol			27.8	28.6		38.5	42.2
n-Propanol Cyclohexanone					30.5		
n-Propanol Thiodiethanol						39.6	44.0

TABLE 5

Comparison of the Surface Tension of Polymers Obtained from Contact Angles, Θ, and from Sedimentation Volumes, V_{sed}

Polymer	Θ_{H_2O} (deg)	Reference	Polymer Surface Tension γ_{SV} (mJ/m^2) from	
			Contact Angle	Sedimentation Volume
PTFE Grade 1 PTFE No.6	104.0±2.0	3	20.0±1.3	20.0 19.7
PVDF	94.8±2.0	This work	25.5±1.3	27.5
PVF	88.6±2.5	This work	29.4±1.7	28.8
HDPE	87.1±2.0	This work	30.3±1.3	29.4
PA 66	70.0±3.0	15	41.1±1.8	39.1
PSF	66.0±2.0	This work	43.1±1.1	43.1

and maximum in the sedimentation volume at $\gamma_{SV} = \gamma_{LV}$. This question will require further study by such means as sedimentation kinetics or direct observations of aggregation.

One further unanswered question is related to adsorption of the liquid components in the liquid/air as well as the solid/liquid interface. In the case of a single component liquid in contact with a polymer particle $\gamma_{LV} = \gamma_{SV}$ implies zero polymer/liquid interfacial tension, γ_{SL}. It is not a priori guaranteed that this is true also for binary liquid mixtures. However, it is interesting to note that experiments of adhesion of biological cells[16] as well as stability of suspensions of fixed red cells in binary liquid mixtures[17] show that these systems behave exactly as one would expect them to behave if the suspending medium would consist of a single component liquid. The two bottom curves in Figure 3, one for a combination of nonpolar and the other for polar liquids also support this finding. In these experiments, significant preferential adsorption of one component in mixtures of n-hexane and n-hexadecane is not to be expected, because of the similarity of the two species. However, it is conceivable that this could be very different in the diethyl ether/tetralin system. Nevertheless, the two curves for the dependence of sedimentation volume on liquid/vapour surface tension are very similar and the position of the minima is, within the experimental error, indistinguishable. This suggests that preferential adsorption of one component in the liquid/air interface, if it occurs, is mimicked by similar adsorption in the solid/liquid interface.

ACKNOWLEDGEMENTS

This work was supported by Energy, Mines and Resources, CANMET, Canada, through contract No. OST83-00132.

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LEGEND OF FIGURES

FIG. 1 Sedimentation volume of PTFE (Grade 1) powder in mixtures of n-hexane/n-hexadecane. Minimum at $\gamma_{LV} = 20.0$ mJ/m^2.

FIG. 2 Sedimentation volume of PTFE (Grade 1) powder in mixtures of diethyl ether/n-hexanol. Maximum at $\gamma_{LV} = 20.2$ mJ/m^2.

FIG. 3 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for polytetrafluoroethylene, PTFE (Grade 1).

FIG. 4 Reproducibility of the sedimentation volume measurements; results from two separate experiments with PTFE (Grade 1) in n-hexane/n-hexadecane. Minima at $\gamma_{LV} = 20.0$ mJ/m^2.

FIG. 5 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for polytetrafluoroethylene, PTFE (No. 6).

FIG. 6 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for polyvinylidenefluoride, PVDF.

FIG. 7 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for polyvinylfluoride, PVF.

FIG. 8 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for high density polyethylene, HDPE.

FIG. 9 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for nylon 66, PA 66.

FIG. 10 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for polysulfon, PSF.

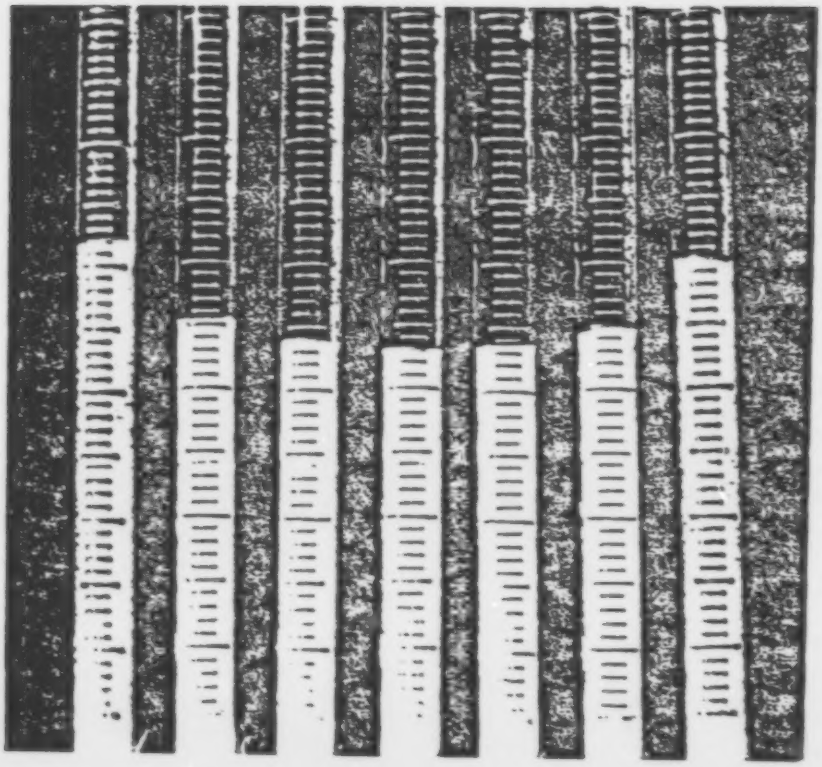

FIGURE 1

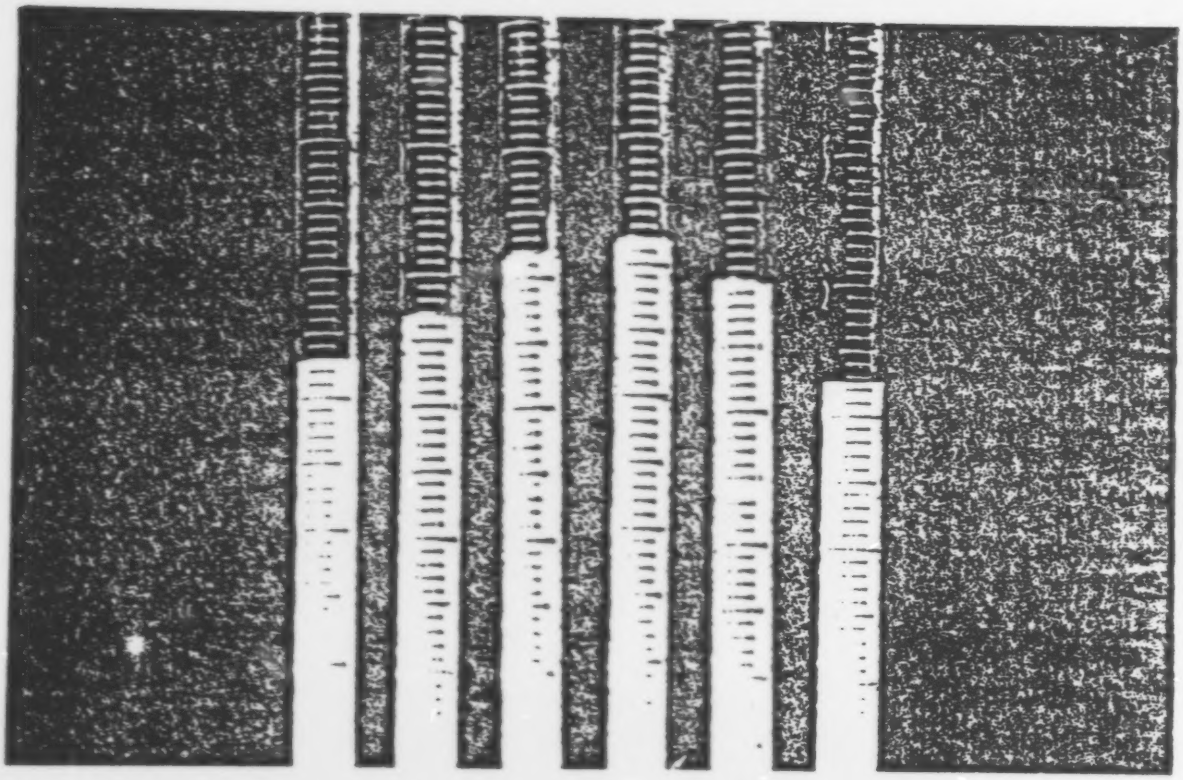

FIGURE 2

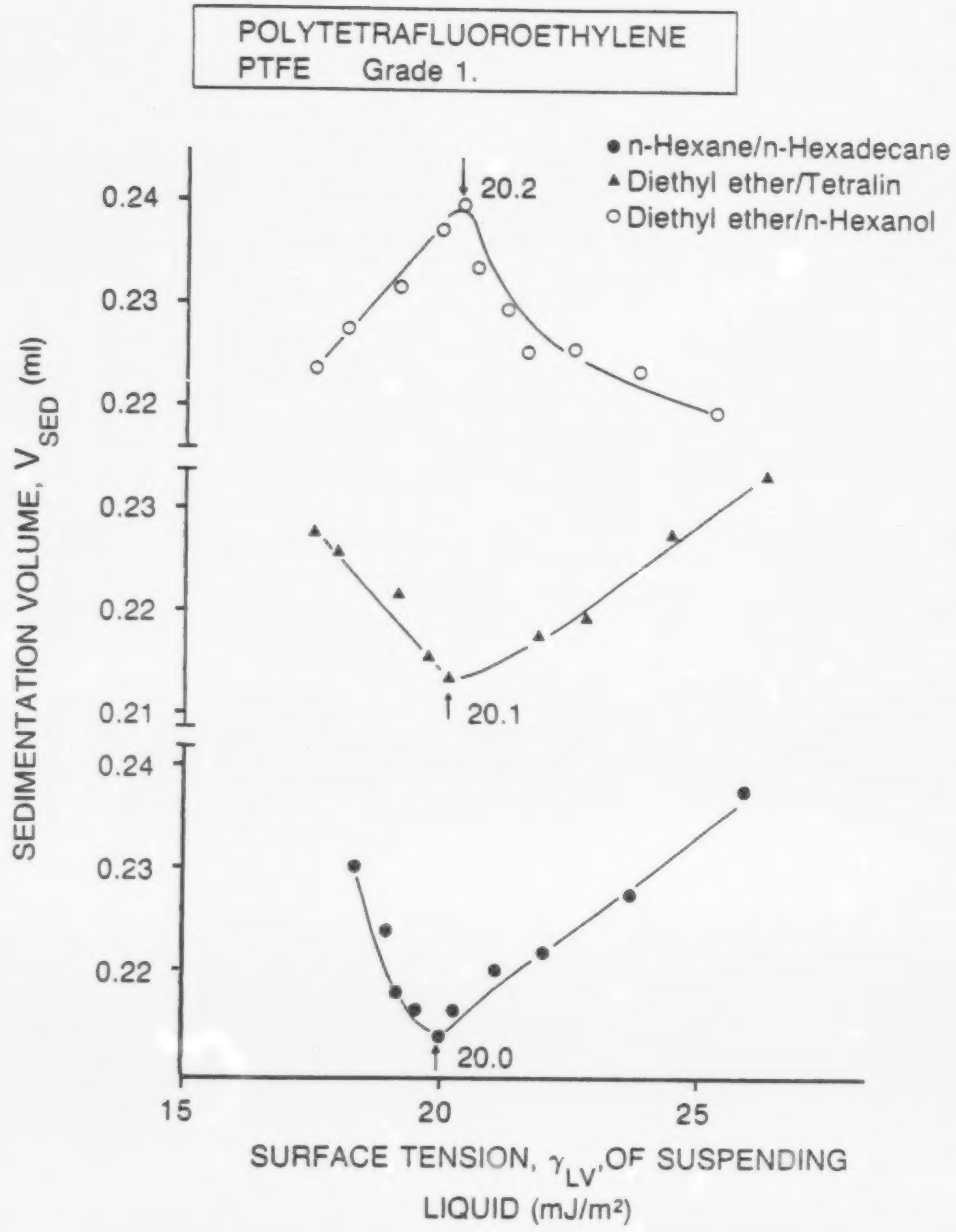
POLYTETRAFLUOROETHYLENE
PTFE Grade 1.
● n-Hexane/n-Hexadecane
▲ Diethyl ether/Tetralin
○ Diethyl ether/n-Hexanol
SEDIMENTATION VOLUME, V_{SED} (ml)
0.24
0.23
0.22
0.23
0.22
0.21
0.24
0.23
0.22
20.2
20.1
20.0
15
20
25
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

FIGURE 3

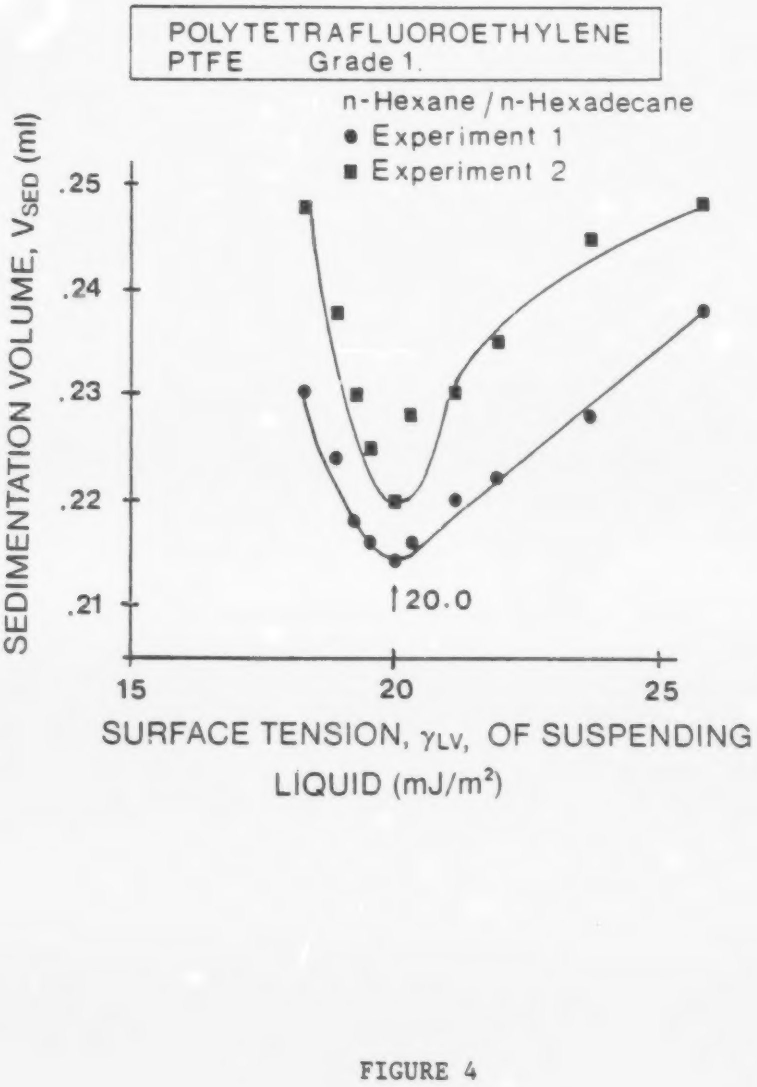
POLYTETRAFLUOROETHYLENE
PTFE Grade 1.
n-Hexane / n-Hexadecane
● Experiment 1
■ Experiment 2
SEDIMENTATION VOLUME, V_{SED} (ml)
.25
.24
.23
.22
.21
20.0
15
20
25
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m^2)

FIGURE 4

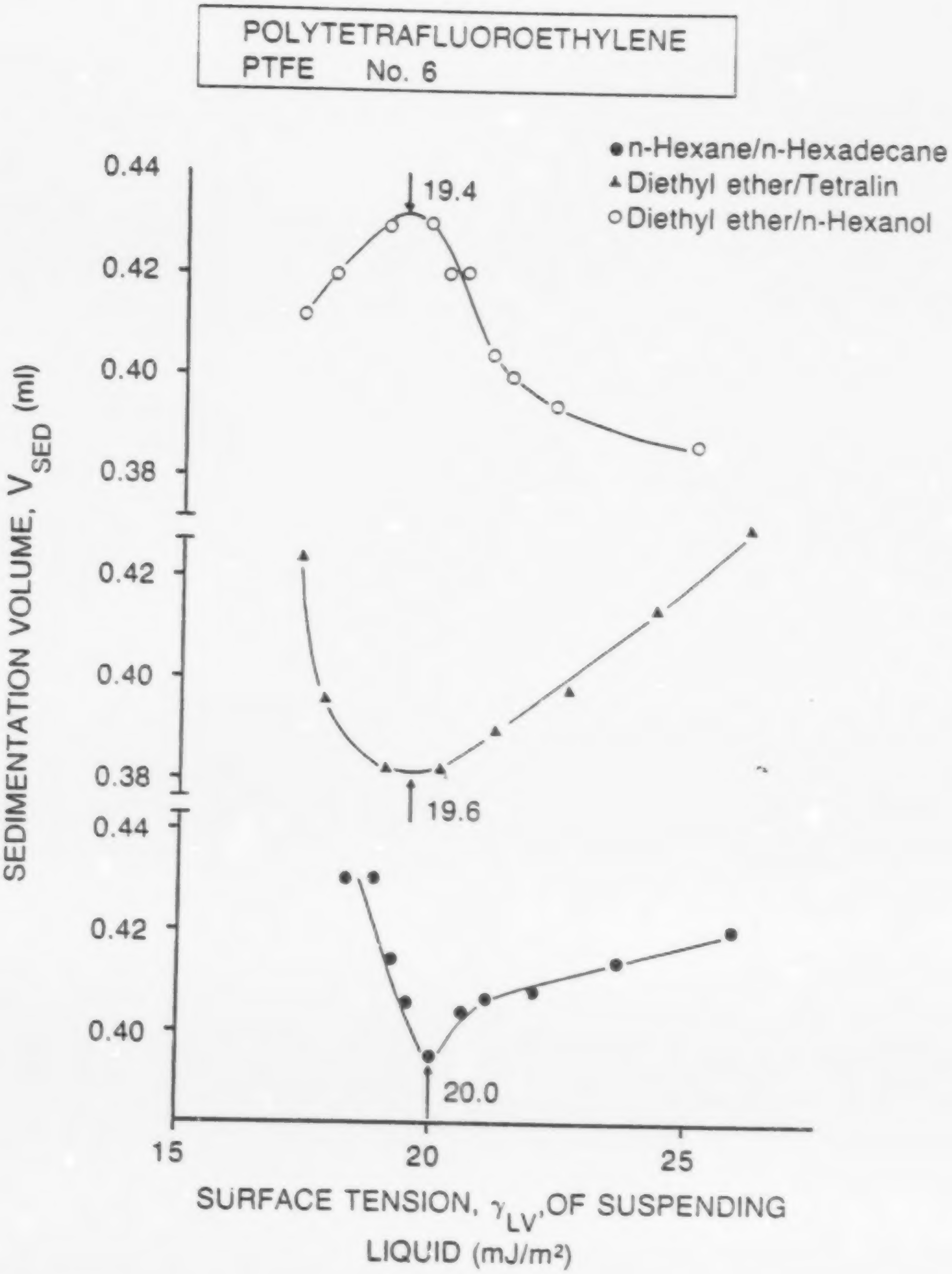POLYTETRAFLUOROETHYLENE
PTFE No. 6
● n-Hexane/n-Hexadecane
▲ Diethyl ether/Tetralin
○ Diethyl ether/n-Hexanol
19.4
19.6
20.0
0.44
0.42
0.40
0.38
0.42
0.40
0.38
0.44
0.42
0.40
SEDIMENTATION VOLUME, V_{SED} (ml)
15
20
25
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

FIGURE 5

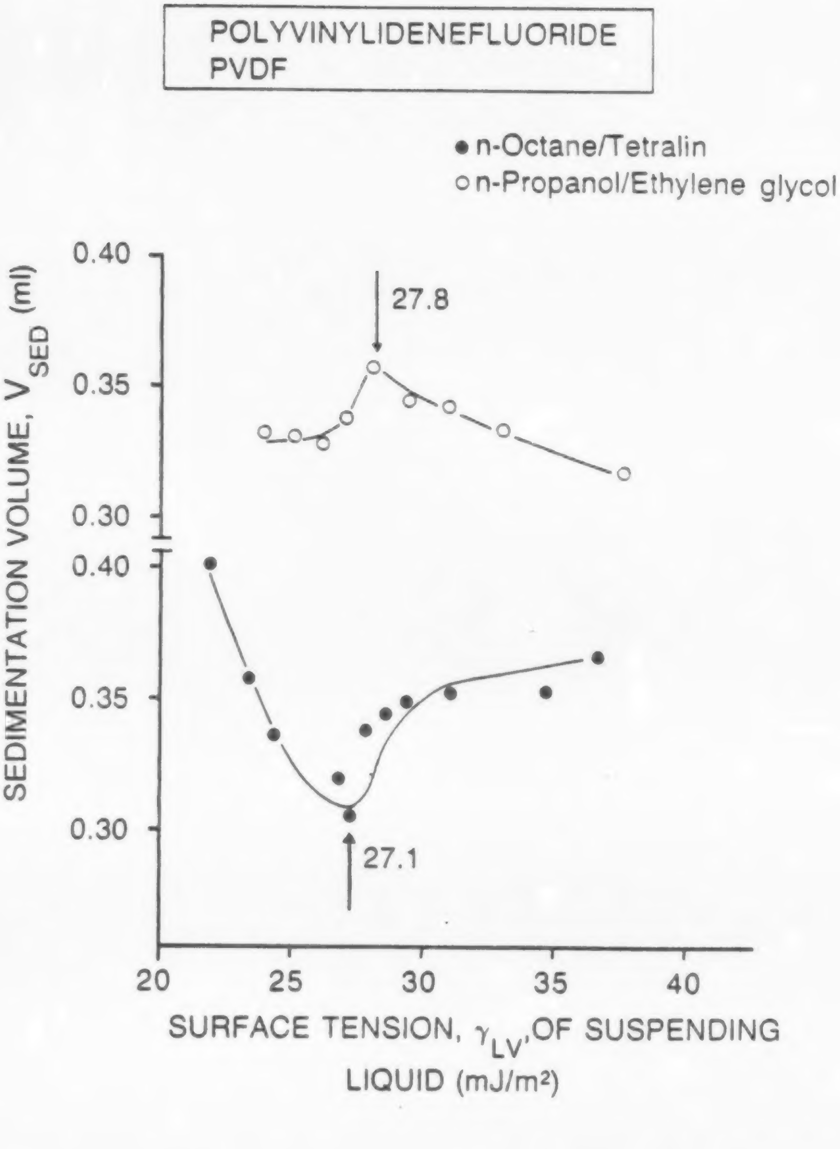
POLYVINYLIDENEFLUORIDE
PVDF
● n-Octane/Tetralin
○ n-Propanol/Ethylene glycol
SEDIMENTATION VOLUME, V_{SED} (ml)
0.40
0.35
0.30
0.40
0.35
0.30
27.8
27.1
20
25
30
35
40
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

FIGURE 6

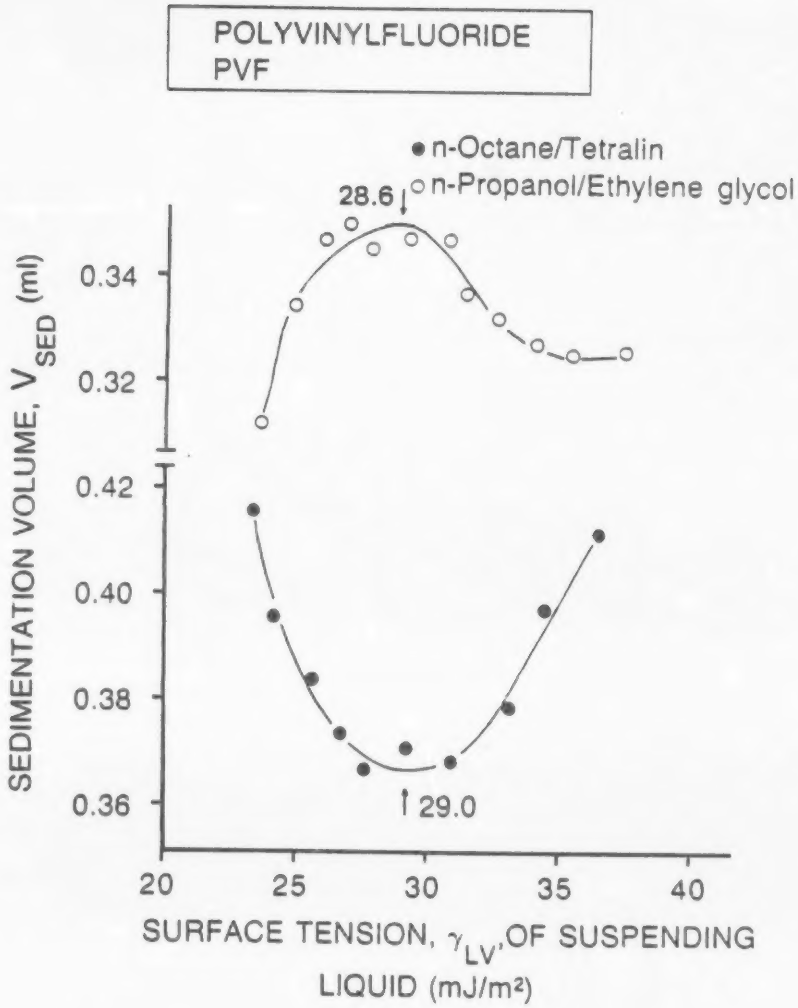
POLYVINYLFLUORIDE
PVF
● n-Octane/Tetralin
○ n-Propanol/Ethylene glycol
28.6
29.0
SEDIMENTATION VOLUME, V_{SED} (ml)
0.34
0.32
0.42
0.40
0.38
0.36
20
25
30
35
40
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

FIGURE 7

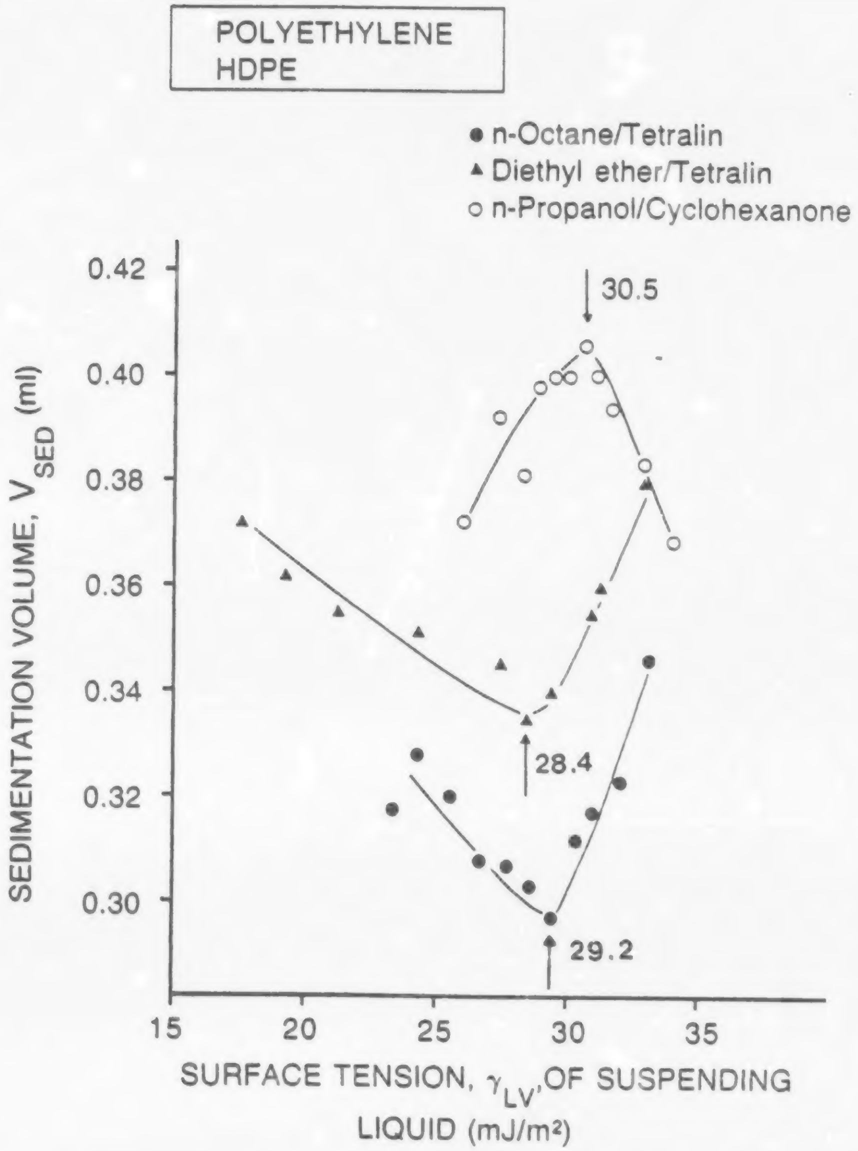
POLYETHYLENE
HDPE
● n-Octane/Tetralin
▲ Diethyl ether/Tetralin
○ n-Propanol/Cyclohexanone
SEDIMENTATION VOLUME, V_{SED} (ml)
0.42
0.40
0.38
0.36
0.34
0.32
0.30
30.5
28.4
29.2
15
20
25
30
35
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

FIGURE 8

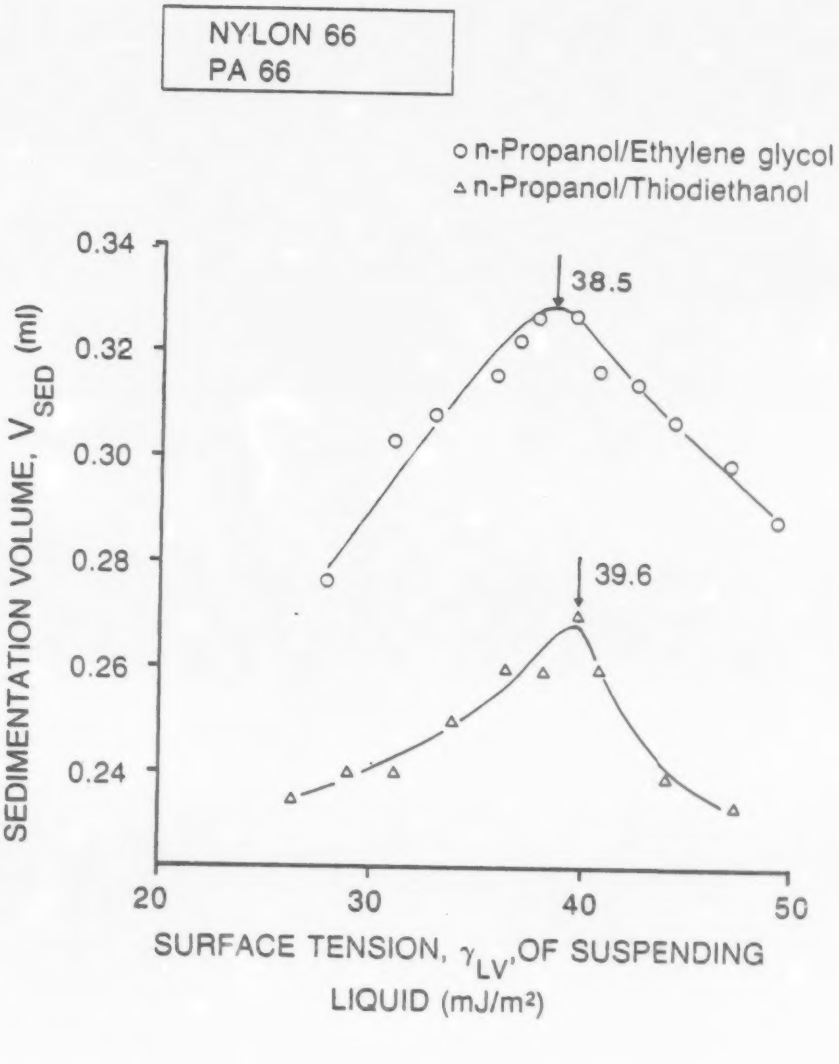
NYLON 66
PA 66
○ n-Propanol/Ethylene glycol
△ n-Propanol/Thiodiethanol
38.5
39.6
0.34
0.32
0.30
0.28
0.26
0.24
20
30
40
50
SEDIMENTATION VOLUME, V_{SED} (ml)
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

FIGURE 9

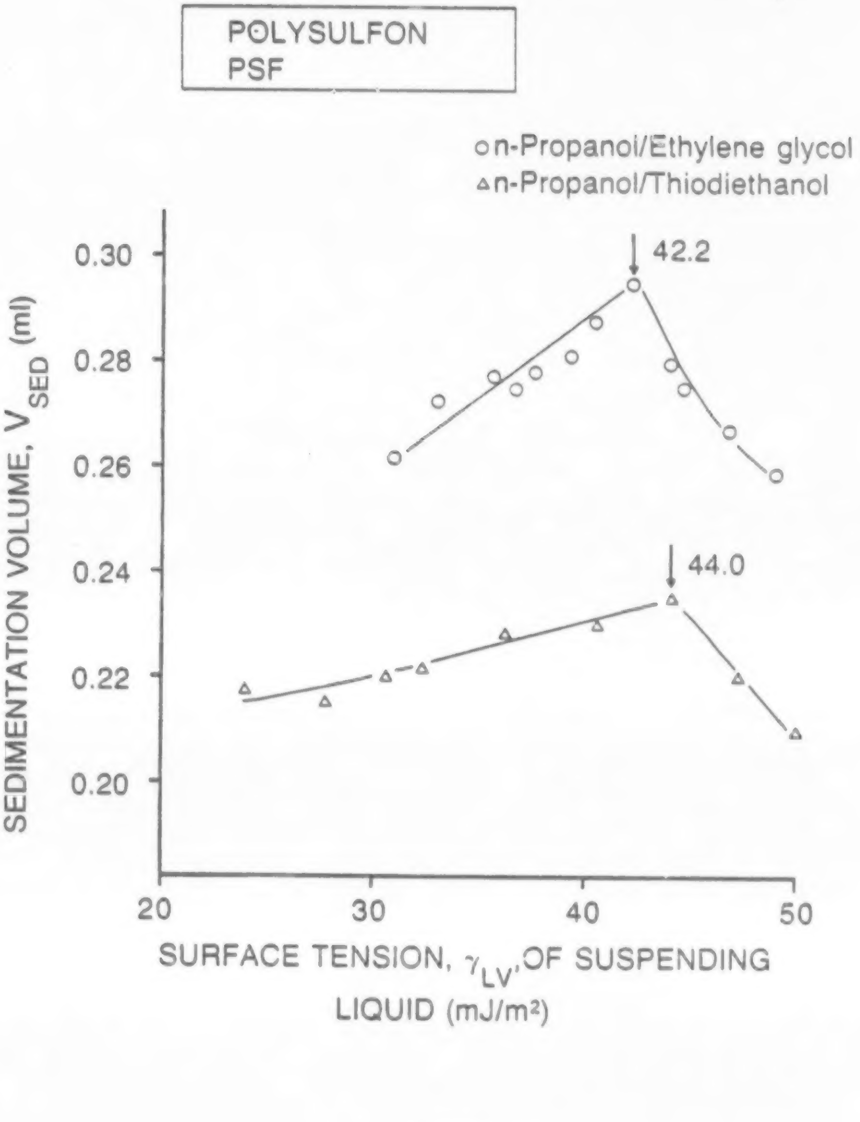
POLYSULFON
PSF
○ n-Propanol/Ethylene glycol
△ n-Propanol/Thiodiethanol
42.2
44.0
0.30
0.28
0.26
0.24
0.22
0.20
SEDIMENTATION VOLUME, V_SED (ml)
20
30
40
50
SURFACE TENSION, γ_LV, OF SUSPENDING LIQUID (mJ/m²)

FIGURE 10

STUDY No. IV

SURFACE TENSION EFFECTS IN THE SEDIMENTATION OF COAL PARTICLES IN VARIOUS LIQUID MIXTURES

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ABSTRACT

The sedimentation volume, V_{sed}, of coal particles in mixtures of pairs of non-polar and more polar organic liquid combinations as well as in aqueous solutions was determined at 20°C.

The liquid combinations were chosen such that the surface tension, γ_{SV}, of the coal particles fell between the surface tensions, γ_{LV}, of the two liquids. A constant mass of a given coal sample was suspended in constant volumes of liquid mixtures of different concentrations.

It was found that the sedimentation volume changed with varying composition of the liquid mixtures, as did the surface tension. A maximum or a minimum occurred in V_{sed} when the surface tension of the suspending liquid was equal to that of the coal particles, i.e. when $\gamma_{LV} = \gamma_{SV}$. Maxima occurred in more polar and minima in the non-polar or less polar liquid mixtures. The position of the extrema, and hence the surface tension, γ_{SV}, of the particles was found to change with particle size, in agreement with findings from other independent techniques.

It was found that the surface tension of coal, γ_{SV}, depends on the surrounding liquid, i.e. coal is hydrophobic in organic and hydrophilic in aqueous media, again in agreement with the results from other techniques.

INTRODUCTION

In the past, ultrafine coal along with refuse material was discarded because of low coal prices and the relatively high recovery costs associated with the processing of fines. However, rising coal prices and the need to meet stringent environmental regulations and economic challenges are factors contributing to the present emphasis on the recovery and the utilization of coal powders.

Froth flotation is the most commonly used technique to separate the fine coal from the associated mineral matter. The wettability of coal particles plays an important role in the recovery of the coal fines in this process.

During the past decade considerable effort has been directed towards the utilization of coal fines in conjunction with fuel oils (Veal and Wall, 1981; Poetschke, 1981; Rowell et al., 1981). The coal-oil and coal-water dispersions have to remain in suspension under the various storage and transportation conditions as well as during utilization. In other words, the stability of the dispersion is of the outmost importance.

Recently, experiments on the sedimentation of polymer particles were performed in our laboratory. The results indicate that from simple sedimentation volume measurements one can establish a correlation between sedimentation volume, particle surface tension and liquid surface tension. These findings also provide insight into the questions of the stability of suspensions and the mechanisms of particle interactions (Vargha-Butler et al., 1984).

It is generally accepted that the stability of a suspension depends to a large degree on the extent of particle-particle interactions which are governed by van der Waals and electrostatic forces (Verwey and Overbeek, 1948). Neumann et al. (1982) have previously discussed the relationship between van der Waals forces and the surface tensions of solids and the interfacial tensions of solid/liquid interfaces. Thus, in view of the relation between surface tension and van der Waals forces, it is to be expected that a correlation between suspension stability and interfacial tensions will be found.

While the van der Waals interactions between unlike solids embedded in a liquid can be attractive as well as repulsive, the interaction between like particles in a liquid can only be attractive or zero. As attraction between solid particles enhances agglomeration and aggregation at given electrostatic interactions, maximum suspension stability will occur when the van der Waals attraction between the particles becomes zero. From theoretical considerations, it is to be expected that this will be achieved when the particle surface tension, γ_{SV}, is equal to the surface tension, γ_{LV}, of the suspending liquid (Neumann et al., 1982). It is of particular interest to consider the sedimentation volume of suspended coal particles in this special case. In order to be able to control and vary the surface tension of the suspending liquids, binary mixtures were chosen of pairs of liquids which span a range of surface tensions including the special case $\gamma_{LV} = \gamma_{SV}$.

In this case, the van der Waals attraction is zero and there are at least two conceivable patterns of behaviour, depending on whether or not agglomeration of the particles at the early stages of sedimentation is possible or not. If agglomeration occurs at finite values of van der Waals attraction, then the degree of agglomeration will decrease when the van der Waals attraction approaches zero. Agglomeration is associated with large sedimentation volumes, because the irregularly shaped aggregates do not pack closely. Therefore, we expect minimum sedimentation volume, V_{sed}, at zero van der Waals attraction. Conversely, when particles are suspended in liquids with different surface tensions and there is initially no agglomeration at finite values of attractive forces, then zero van der Waals attraction implies least close packing of the sediment and hence a maximum of V_{sed}.

For polymer powders, both types of extrema were observed (Vargha-Butler et al., 1984). It was found that the type of extremum at $\gamma_{LV} = \gamma_{SV}$ depends on the polarity of the suspending liquids; minima occurred in non-polar liquids and maxima were found in more polar liquid combinations. The results obtained for polymers encouraged us to study suspensions of coal powders from the same point of view.

In recent years, the surface tension, γ_{SV}, of coal powders was determined in our laboratory by means of the solidification front method in organic media (Soulard, 1980; Vargha-Butler et al., 1981; Soulard et al., 1983; Vargha-Butler et al., 1984) as well as in aqueous media (Neumann et al., 1984). Absolom et al. (1984) employed the adhesion technique in order to determine the surface tension of coal particles in both organic and aqueous systems.

The latter studies (Neumann et al., 1984; Absolom et al., 1984) uncovered a peculiar pattern of the interaction of coal with the suspending liquids. Under the same experimental conditions, inert materials such as polymer particles exhibit a unique surface tension regardless of the nature of the suspending liquids. However, coal does not; instead, the effective surface tension of coal seems to vary depending on the liquid medium with which it is in contact. In essence, coal is relatively hydrophobic, with a surface tension typically in the range of 30-45 mJ/m^2, in organic liquids whereas it is hydrophilic, having a surface tension near 70 mJ/m^2, in water or in aqueous media. The duality of response to organic and aqueous liquids has an immediate bearing on practical aspects of coal processing and utilization. It suggests that the response of coal to aqueous media cannot be anticipated from its response to non-aqueous ones. It also suggests that the hydrophobic nature of the coal is greatly reduced when the coal particles are immersed in aqueous media.

The purpose of the present paper is to study the sedimentation behaviour of coal fines and, in particular, to examine the effect of the polarity of the suspending liquids on the type of extremum as well as o[illegible]e resultant surface tension of the coal particles. The partic[illegible]ze dependence in non-aqueous dispersions will also be examined. Furthermore, sedimentation experiments will be performed in aqueous media to explore the duality of the coal surface tension further. Results from the sedimentation experiments will be compared with the surface tensions obtained from solidification front and adhesion measurements.

EXPERIMENTAL

1. Materials

1.1 Coal Samples

The sedimentation experiments were performed with six coals from Western Canada and one coal originating from Nova Scotia, Eastern Canada. Five of the coals are bituminous, while coal No. 3 and the sample from the Wabamun Lake area are subbituminous. The origin, rank, date of mining, the type of sizing and the density of the coal samples are given in Table I.

The samples were provided by EMR, CANMET, Coal Research Laboratory, Edmonton, Alberta. All of the coals had been ground, dry or wet screened and dried at ambient temperature. The coal samples were stored at room temperature in well sealed bottles and were not exposed to light or heat.

Each coal sample consisted of five size fractions identified by a mesh range (-60+100, -100+200, -200+325, -325+400 and -400 mesh). In most cases, coal samples with a size fraction of -400 mesh were used for the sedimentation experiments.

Two sets of sedimentation experiments were performed with coal fractions of larger particle size in order to study the effect of the particle size on sedimentation volume extrema and particle surface tension.

1.2 Suspending Liquid Mixtures

The sedimentation volume, V_{sed}, of the coal powders was determined in mixtures of pairs of non-polar as well as more polar liquid combinations. The majority of the liquids used were organic solvents, but experiments were also performed in aqueous solutions of dimethylsulfoxide (DMSO). The liquid combinations were chosen such that the surface tension, γ_{L_1V}, of one liquid was lower than the surface tension of the coal particles, while that of the second liquid, γ_{L_2V}, was higher.

There are several conditions which the suspending liquids must satisfy in order to be suitable for sedimentation volume experiments. The criteria for choosing liquid components are: (1) they should be chemically inert with respect to the solid particles and should not dissolve the particles or components thereof; (2) the boiling temperature should be reasonably high to minimize evaporation; (3) the density of the liquids should be less than that of the particles; (4) liquids with a zero or nearly zero dipole moment as well as those with a higher dipole moment should be used in order to cover a wide polarity range; (5) the liquid components should be miscible with each other in all volume ratios; and (6) the surface tension, γ_{LV}, of the liquid mixtures should cover the surface tension range required.

For the sedimentation experiments performed with various polymer powders (Vargha-Butler et al., 1984), several liquid combinations were used which were selected according to the aforementioned criteria. In the case of coal sedimentation, however, the first criterion might not be easily satisfied. Chemically, coal is considerably more complex and heterogeneous than polymers and less resistant to organic liquids. Some components of coal can easily be dissolved by solvents; in some cases, such effects were experimentally observed as a discolouration of the supernatant liquid.

Eighteen liquids with known density, dipole moment and surface tension were selected for the sedimentation experiments. These liquids were Aldrich, Baker and/or Fluka reagents (certified laboratory grade).

The sedimentation volume, V_{sed}, of coal was measured with the following fifteen pairs of non-polar and polar liquid combinations:

(1) n-octane/decalin
(2) cyclohexane/decalin
(3) n-octane/tetralin (1,2,3,4 tetrahydronaphthalene)
(4) benzene/chlorobenzene
(5) benzene/1,2,4 trichlorobenzene
(6) n-hexane/cyclohexanone
(7) methanol/1,2 propanediol
(8) methanol/ethylene glycol (1,2 ethanediol)
(9) methanol/formamide
(10) n-propanol/2,2' thiodiethanol
(11) n-propanol/ethylene glycol
(12) n-propanol/formamide
(13) n-propanol/DMSO (dimethylsulfoxide)
(14) acetone/ethylene glycol, and
(15) DMSO/water

Prior to the sedimentation measurements, the liquid/vapour surface tension, γ_{LV}, of the different liquid compositions as well as that of the pure solvents was determined by means of the modified Wilhelmy plate method (Neumann and Good, 1979) at 20°C. The values of the surface tensions of the pure liquids obtained in this manner showed good agreement with the literature data.

2. Method

Determination of the Sedimentation Volume, V_{sed}

Prior to the actual sedimentation experiments, the coal powders were thoroughly agitated in the appropriate liquids in order to break up any aggregates and to displace air bubbles. For this purpose, a specified mass of a given coal sample was weighed into small polyethylene micro centrifuge tubes with tight fitting caps. The mass of coal powder used per tube varied from 0.05 to 0.10 grams depending on the density, the particle size and the compactness of the coal powders. The choice of the amount of coal particles for any set of experiments was essentially one of convenience and practicality. It proved to be desirable, from the point of view of accuracy and precision, to have the maximum sedimentation volume in a series of experiments approximately equal to one half of the total volume of the sedimentation tube. In general, we used 0.05 grams of coal from the -400 mesh fractions and 0.08 or 0.10 grams from fractions of larger particle sizes.

In this series of experiments, since we were interested only in determining at which liquid/liquid combination the sedimentation extremum occurs, it was not necessary to employ exactly the same mass of coal in each case. It is the relative position of the V_{sed} extremum which is important - the absolute value of V_{sed} is not required. The sample mass was weighed with analytical accuracy. The coal powders in the centrifuge tubes were then suspended in approximately 0.1 to 0.2 ml of the liquid mixtures with different compositions by agitating the samples for at least five minutes using a Vortex test tube mixer. In order to achieve as much displacement of air as possible, the samples were left for twenty four hours and then agitated again for another five minutes.

For the actual sedimentation experiments, graduated, 1 ml Wintrobe micro test tubes (100 mm high with an inner diameter of 3 mm) were used. These graduated tubes can be read to an accuracy of 0.001 ml.

Each of the dispersions prepared in the centrifuge tubes was then transferred into the Wintrobe tube using Pasteur micropipettes. The appropriate liquid mixture was used as rinsing liquid in each case. Finally, the microtubes were filled up to a constant volume of 1.00 ml with the appropriate liquid mixture. The microtubes were then sealed and shaken for approximately five minutes so that the coal powder was totally and homogeneously suspended in the liquid column. The reading of the sedimentation volume, V_{sed}, of the coal powder was taken every day for three days to one week, depending on the sample, until no further change in V_{sed} occurred.

RESULTS AND DISCUSSION

1. Sedimentation in Organic Media

Photographs of the sedimentation volume of B.C. coal powder (-400 mesh fraction) suspended in liquid pairs of n-octane/tetralin and of n-propanol/DMSO of varying concentration and hence surface tension are shown in Figures 1 and 2, respectively. In Figure 3, the same sedimentation volumes, V_{sed}, are plotted as a function of the surface tension, γ_{LV}, of the suspending liquids. Data for two additional systems, i.e. B.C. coal in n-propanol/ethylene glycol and in methanol/1,2 propanediol are also given in Figure 3.

The final sedimentation volume, V_{sed}, changes with varying composition of the liquid mixtures, as does the liquid surface tension, γ_{LV}, such that V_{sed} exhibits an extremum at a certain liquid surface tension. It is apparent that this extremum is a minimum in the case of non-polar or slightly polar binary liquid combinations such as n-octane/tetralin (Figures 1 and 3). In the case of more polar liquids such as the mixtures of n-propanol/DMSO, n-propanol/ethylene glycol or methanol/1,2 propanediol, the extrema are maxima (Figures 2 and 3). Similar plots were obtained for the other six coal samples investigated, in various organic liquid combinations. These results are given in Figures 4 to 9.

Since a detailed and complete error analysis of such data would require an unmanageable amount of work, we restrict ourselves to giving, in Figure 10 (and for experiments with aqueous media in Figure 14), results for two separate experiments for B.C. coal in the n-propanol/DMSO system. Although the two curves are not identical, they are similar. They both show a maximum which occurs at γ_{LV} = 28.5 mJ/m^2 in experiment 1 and at γ_{LV} = 27.1 mJ/m^2 in experiment 2. In the case of polymers, the position of the extrema was much more reproducible. For coals, the surface tension, γ_{LV}, of the suspending liquid at which extrema occur may vary as much as 1.5 mJ/m^2 after repeating the sedimentation with the same system, depending on the actual coal sample.

The type of extremum of the sedimentation volume obtained for six of the coal samples in the various liquid combinations is given in Table II together with the surface tension and dipole moment range of the liquid pairs. The surface tensions, γ_{LV}, of the liquid mixtures at which the extrema occur are summarized in Table III for the same six coals. All relevant data for the seventh coal, sample No. 1, which was more extensively studied than the other coals, are summarized in Table IV.

From the results of Tables III and IV, two significant facts can be deduced. We have previously observed during sedimentation experiments with polymer powders (Vargha-Butler et al., 1984) that the acquisition of a minimum in the sedimentation volume does not require a completely non-polar liquid mixture with a dipole moment equal to zero, such as n-hexane/n-hexadecane, n-octane/decalin or cyclohexane/decalin. If one or both of the two components of the suspending liquid has a finite but small dipole moment, as is the case for n-octane/tetralin or benzene/chlorobenzene, the sedimentation volume extremum will still be a minimum, and not a maximum. Since our hypothesis stipulates a minimum in a system where particles are aggregated at finite values of the van der Waals attraction, there might be a "threshold" value of polarity below which the particle aggregation is favorable.

It was observed in polymer particle sedimentation that, for the same polymer in different liquid combinations, the position of the minima and maxima is almost identical (Vargha-Butler et al., 1984). However, the results obtained for one and the same coal sample in systems with different polarity (see Tables III and IV) show that the extremum of the sedimentation volume is generally shifted to a higher surface tension, γ_{LV}, of the liquid composition with increasing polarity of the suspending liquid.

These results suggest that the surface tension of coal is, in fact, different in the different liquid systems, possibly due either to the elution of individual components of coal or to the preferential adsorption of one liquid component. The position of the sedimentation volume extremum and, by implication, the surface tension of the coal samples are not strictly independent of liquid properties (cf. Table IV). For comparison purposes, the range of particle surface tensions for the different coal samples obtained from V_{sed} in the different liquid mixtures is listed in Table V. This table also contains the particle surface tension, γ_{SV}, obtained from solidification front experiments using thymol as the matrix material. The surface tension of coal

No. 3 and B.C. coal obtained from solidification front experiments were reported previously (Vargha-Butler et al., 1984 and Neumann et al., 1984). The results for DEVCO coal were summarized by Dong Ho Lee (1984). The data summarized in Table V refer to the surface tension of particles with a -400 mesh size (particles less than 37 μm in diameter) at 20°C.

While, in the case of polymer particles, such comparisons between sedimentation volume extremum and γ_{SV} measurements by other means yielded close agreement, this is not so in the present study, presumably due to the heterogeneous character of coal.

2. Particle Size Effects in Coal Sedimentation

It was reported earlier (Soulard, 1980; Vargha-Butler et al., 1981; Soulard et al., 1983) that the surface tension of coal, γ_{SV}, increases with increasing particle size. Therefore, two types of coals, the bituminous B.C. coal and a subbituminous sample from Wabamun Lake were investigated by the sedimentation technique as a function of particle size. Four fractions (-100+200, -200+325, -325+400 and -400 mesh) of B.C. coal were investigated in n-propanol/ethylene glycol mixtures. The sedimentation volumes as a function of the surface tension, γ_{LV}, of the suspending liquid are given in Figure 11. Similar plots for the three fractions of Wabamun Lake coal (-200+325, -325+400 and -400 mesh size) measured in n-propanol/DMSO are shown in Figure 12. In both cases, the surface tension, γ_{LV}, corresponding to the maximum V_{sed} increases with increasing particle size in agreement with the results obtained from solidification front experiments.

A comparison between the results obtained from solidification front and sedimentation measurements is given in Table VI. We note that, for small particles, the surface tension values obtained from sedimentation are significantly smaller than those obtained from the solidification front technique. However, it is remarkable that for the largest particles the results obtained from the two approaches are in very close agreement. These patterns of behaviour are not completely understood at the present time.

This particle size dependence of surface tension was not observed with homogeneous solid particles (e.g. polymer powders), in either the solidification (Vargha-Butler et al., 1984) or sedimentation volume techniques (Vargha-Butler et al., 1984). In the case of coal it was found that not only the surface tension but other physical properties, e.g. density, specific heat (Vargha-Butler et al., 1982) also vary as a function of particle size. We attributed this dependence on size to the varying degrees of heterogeneity of the coal powders. Mineral components (clays, oxides, carbonates, sulfides, etc.) after grinding and sizing can be distributed in different concentrations in the coal fractions.

3. Coal Sedimentation in Aqueous Media

Solidification front experiments with coal particles in organic matrix materials and in water revealed that the surface properties of coal are not unique, in contrast to the situation with polymer particles. Coal is hydrophobic in organic media and hydrophilic in aqueous media (Neumann et al., 1984). The same pattern emerged when determinations of the surface tension of coal particles were made by means of the adhesion technique (Absolom et al., 1984). Therefore, we wanted to investigate whether this duality could also be observed by performing sedimentation volume measurements with coal in aqueous media.

Two bituminous (B.C. and DEVCO) coals and one subbituminous (No. 3) coal were studied in aqueous mixtures of DMSO. A photograph of the sedimentation volume of DEVCO coal (-400 mesh fraction) suspended in mixtures of DMSO/water is shown in Figure 13. The results of two separate experiments illustrating the reproducibility for the same coal are given in Figure 14. Similar experiments were performed for B.C. (Figure 15) and No. 3 (Figure 16) coal samples.

Both components of the binary mixture of DMSO/water are highly polar liquids with a dipole moment of 6.24×10^{-30} (Cm) for water and of 13.21×10^{-30} (Cm) for DMSO. The sedimentation volume, as expected, shows a maximum for each of the three coal samples.

The particle surface tension, γ_{SV}, of coal fractions below 400 mesh, obtained from sedimentation, solidification front and adhesion techniques in aqueous media, are compared in Table VII. The surface tension of the two bituminous coal samples range from 68.6 to 70.9 mJ/m^2 regardless of the method (sedimentation or adhesion technique) and the liquid combination (DMSO/water or n-propanol/water). The subbituminous coal No. 3 has a somewhat lower surface tension. The agreement between data from sedimentation and adhesion measurements is excellent.

The particle surface tensions obtained from solidification front experiments in water/ice are almost identical for the three coal samples and are higher (72.1 ± 0.3 mJ/m^2) than those obtained from the sedimentation or adhesion studies. We suggested recently (Neumann et al., 1984) that coal particles immersed in water are highly hydrated and their surface tension, γ_{SV}, is, therefore, virtually that of water. On the other hand, in binary liquids with one organic component (i.e. the case of sedimentation as well as adhesion experiments), the surface tension of the particles varies somewhat in the different mixtures. There is the possibility that preferential adsorption of the organic compounds, leading to a somewhat lower surface tension, may occur. An alternative explanation is that the various liquid mixtures may selectively elute different components from the coal samples giving rise to samples with varying surface tensions. As colour changes of the supernatant are frequently observed it appears that such an effect exists.

CONCLUSIONS

From the results of sedimentation experiments performed with coal powders in various liquid mixtures, we conclude:

1. The sedimentation technique is a useful tool for studying particle-particle interactions and suspension stability in connection with the surface tension of coal fines.
2. The sedimentation volume of coal varies with the composition and hence with the surface tension of the suspending binary liquids, showing an extremum at a certain liquid surface tension.
3. The type of extremum (minimum or maximum) depends on the polarity of the suspending liquid mixtures. In non-polar or slightly polar systems, minima are observed and in more polar liquids maxima occur. The extrema occur where $\gamma_{LV} = \gamma_{SV}$, i.e. at zero van der Waals attraction.
4. The surface tension, γ_{SV}, of coal, as judged by the position of the sedimentation volume extremum, increases somewhat with increasing polarity of the binary liquids.
5. The surface tension of coal as judged by the location of sedimentation volume extrema shows a particle size dependence. The surface tension values for small particles are significantly lower than those obtained for larger particles. This size dependence is in

agreement with results obtained from the solidification front technique. However, in the case of small particles, the surface tension values obtained from V_{sed} are somewhat lower than those obtained with the solidification front method for the same size fraction. With increasing particle size, the results from the two techniques approach each other and agree very well for the largest particles.

6. The sedimentation results support the previous observation of a dualistic behaviour of coal: in organic media coal is hydrophobic and in aqueous media it is hydrophilic.

ACKNOWLEDGEMENTS

This work was supported by Energy, Mines and Resources, CANMET, Canada, through Contract No. OST83-00132.

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LEGENDS OF FIGURES

Figure 1 Sedimentation volume of B.C. coal powder (-400 mesh) in mixtures of n-octane/tetralin. Minimum at $\gamma_{LV} = 30.2\ mJ/m^2$.

Figure 2 Sedimentation volume of B.C. coal powder (-400 mesh) in mixtures of n-propanol/DMSO. Maximum at $\gamma_{LV} = 28.5\ mJ/m^2$.

Figure 3 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for B.C. coal (-400 mesh).

Figure 4 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for DEVCO coal (-400 mesh).

Figure 5 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for CARDINAL RIVER coal (-400 mesh).

Figure 6 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for COAL VALLEY coal (-400 mesh).

Figure 7 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for coal No. 1 (-400 mesh).

Figure 8 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for coal No. 3 (-400 mesh).

Figure 9 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for WABAMUN LAKE coal (-400 mesh).

Figure 10 Reproducibility of the sedimentation volume measurements in organic medium; results from two separate experiments with B.C. coal (-400 mesh) in n-propanol/DMSO. Maxima at γ_{LV} = 27.1 and 28.5 mJ/m^2, respectively.

Figure 11 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for different size fractions of B.C. coal in n-propanol/ethylene glycol.

Figure 12 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for different size fractions of WABAMUN LAKE coal in n-propanol/DMSO.

Figure 13 Sedimentation volume of DEVCO coal powder (-400 mesh) in mixtures of DMSO/water. Maximum at γ_{LV} = 68.8 mJ/m^2.

Figure 14 Reproducibility of the sedimentation volume measurements in an aqueous medium; results from two separate experiments with DEVCO coal (-400 mesh) in DMSO/water. Maxima at γ_{LV} = 68.8 and 69.3 mJ/m^2, respectively.

Figure 15 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for B.C. coal (-325+400 mesh) in DMSO/water.

Figure 16 Sedimentation volume, V_{sed}, as a function of the surface tension, γ_{LV}, of the suspending liquid for coal No. 3 (-400 mesh) in DMSO/water.

TABLE I

Origin, rank, type of sizing and density of coal samples

Coal Sample	Origin	Rank and Date of Mining	Type of Sizing	Density ρ (kg/m^3)
B.C.	Kaiser Resources Harmer Seam Pit 29 South British Columbia	bituminous 1982	dry screened	1410
DEVCO	Sidney Nova Scotia	bituminous high-volatile 1982	dry screened	1370
CARDINAL RIVER	Hinton Alberta	bituminous 1982	dry screened	1320
COAL VALLEY	Mynheer A Seam Coal Valley Alberta	bituminous 1983	dry screened	1445
NO.1	Quintette Area Northeastern British Columbia	bituminous medium-volatile 1979	wet screened	1520
NO.3	Judy Creek Area Northern Alberta	subbituminous 1979	wet screened	1630
WABAMUN LAKE	Wabamun Lake Alberta	subbituminous 1983	dry screened	1400

TABLE II

Type of extremum of sedimentation volume, V_{sed}, for the coal samples investigated in liquids of different polarity

Liquid Pairs Used for Sedimentation	Surface Tension Range γ_{LV} (mJ/m^2)	Dipole Moment Range $\mu x10^{-30}$ (Cm)	Type of V_{sed} Extremum Obtained for					
			B.C.	DEVCO	CARDINAL RIVER	COAL VALLEY	NO.3	WABAMUN LAKE
n-Octane/Tetralin	21.8/36.5	0 / 1.63	min	min	min	min	min	min
n-Hexane/Cyclohexanone	18.3/34.3	0 / 9.01	min					
n-Propanol/Ethylene glycol	23.8/48.9	5.60/ 7.61	max		max	max	max	max
n-Propanol/Thiodiethanol	23.8/52.5	5.60/ ?		max				
Methanol/1,2 Propanediol	23.5/35.9	5.67/ 7.51	max					
n-Propanol/Formamide	23.8/59.9	5.60/12.44		max				
n-Propanol/DMSO	23.8/44.3	5.60/13.21	max		max	max	max	max

TABLE III

Extrema of sedimentation volumes for coal fractions below 400 mesh in different liquid combinations

	Surface Tension, γ_{LV} (mJ/m^2), at which Extremum Occurs for Coal Samples					
Liquid Combinations	B.C.	DEVCO	CARDI-NAL RIVER	COAL VALLEY	NO.3	WABA-MUN LAKE
n-Octane/Tetralin	30.2	33.0	30.2	31.0	28.5	30.2
n-Hexane/Cyclohexanone	31.0					
n-Propanol/Ethylene glycol	27.8		35.4	35.9	31.5	30.7
n-Propanol/Thiodiethanol		35.1				
Methanol/1,2 Propanediol	29.1					
n-Propanol/Formamide		35.4				
n-Propanol/DMSO	28.5		34.5	35.2	35.9	31.5

TABLE IV

Extrema of sedimentation volumes, V_{sed}, for Coal No.1 in liquids of different polarity

Liquid Pairs Used for Sedimentation	Surface Tension Range γ_{LV} (mJ/m^2)	Dipole Moment Range $\mu x10^{-30}$ (Cm)	V_{sed} Extremum at γ_{LV} of Liquids	
			Type	γ_{LV} (mJ/m^2)
n-Octane/Decalin	21.8/32.3	0 / 0	min	28.4
Cyclohexane/Decalin	24.9/32.3	0 / 0	min	28.7
Benzene/Chlorobenzene	28.9/33.6	0 / 5.64	min	32.4
Benzene/1,2,4 Trichlorobenzene	28.9/39.7	0 / ?	min	33.1
Methanol/Ethylene glycol	23.5/48.9	5.67/ 7.61	max	33.4
Acetone/Ethylene glycol	22.6/48.9	9.61/ 7.61	max	34.6
Methanol/Formamide	23.5/59.9	5.67/12.44	max	33.9

TABLE V

Particle surface tension, γ_{SV}, of coal fractions below 400 mesh obtained from the solidification front and sedimentation volume techniques in organic media

Coal Sample -400 Mesh	Particle Surface Tension γ_{SV} at 20°C (mJ/m^2) from Solidification Front	Sedimentation Volume
B.C.	38.7	27.8 - 31.0
DEVCO	36.4	33.0 - 35.4
CARDINAL RIVER	39.5	30.2 - 35.4
COAL VALLEY	37.5	31.0 - 35.9
NO.1	37.3	28.4 - 34.6
NO.3	38.4	28.5 - 35.9
WABAMUN LAKE	36.9	30.2 - 31.5

TABLE VI

Particle size dependence of surface tension, γ_{SV}, of coal obtained from solidification front and sedimentation volume techniques in organic media

Coal Sample	D	Particle Surface Tension, γ_{SV} (mJ/m^2), at 20°C from Solidification Front		Sedimentation Volume	Mesh Fraction
	(μm)	γ_{SV}	Mean γ_{SV}	Mean γ_{SV}	
B.C.	15	37.8	38.7	27.8	-400 (D < 37μm)
	30	39.6			
	30	39.6	40.2	31.5	-325+400 (37μm< D <44μm)
	45	40.7			
	45	40.7	41.5	35.9	-200+325 (44μm< D <74μm)
	60	41.5			
	75	42.2			
	75	42.2	43.6	44.0	-100+200 (74μm< D <149μm)
	90	42.9			
	120	44.0			
	150	45.3			
WABAMUN LAKE	15	36.2	36.9	31.5	-400 (D < 37μm)
	30	37.5			
	30	37.5	38.0	34.1	-325+400 (37μm< D <44μm)
	45	38.5			
	45	38.5	39.1	39.3	-200+325 (44μm< D <74μm)
	60	39.2			
	75	39.7			

TABLE VII

Particle surface tension, γ_{SV}, of coal fractions below 400 mesh obtained from the solidification front, sedimentation volume and adhesion techniques in aqueous media

Coal Sample -400 mesh	Particle Surface Tension, γ_{SV}, (mJ/m^2), at 20°C Obtained from			
	Solidification Front in Water/Ice	Sedimentation Volume in DMSO/Water	Particle Adhesion in DMSO/Water	Particle Adhesion in n-Propanol/Water
B.C.	71.8	70.9	-	69.0
DEVCO	72.1	69.0	68.6	69.1
NO.3	72.3	64.4	-	64.9

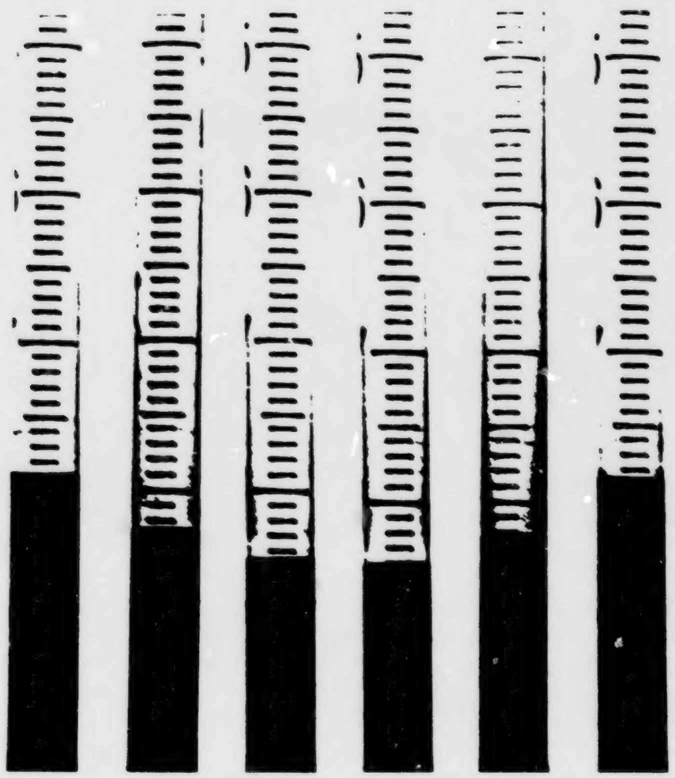


Figure 1

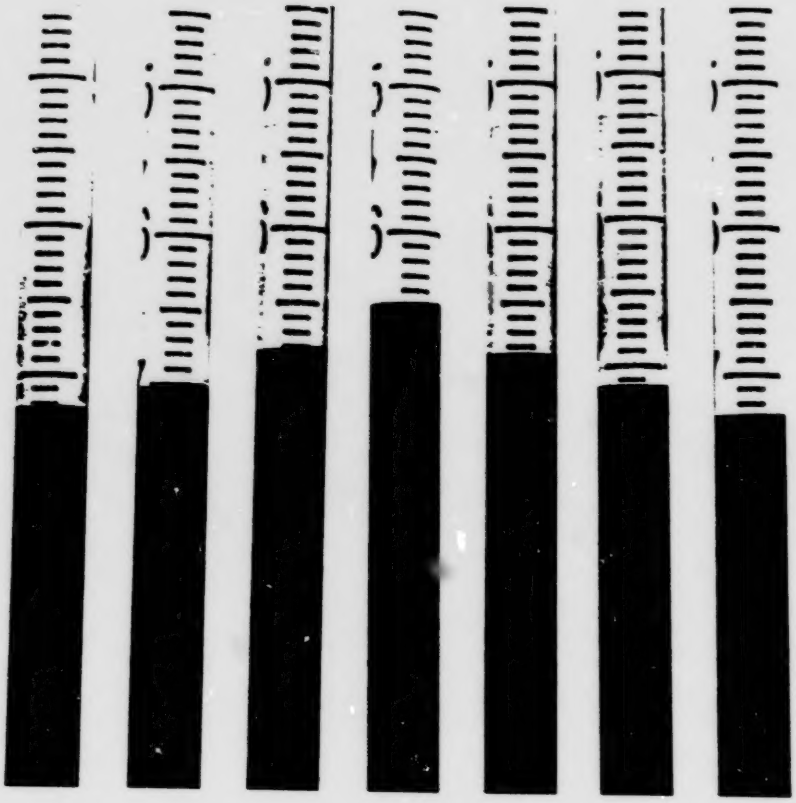


Figure 2

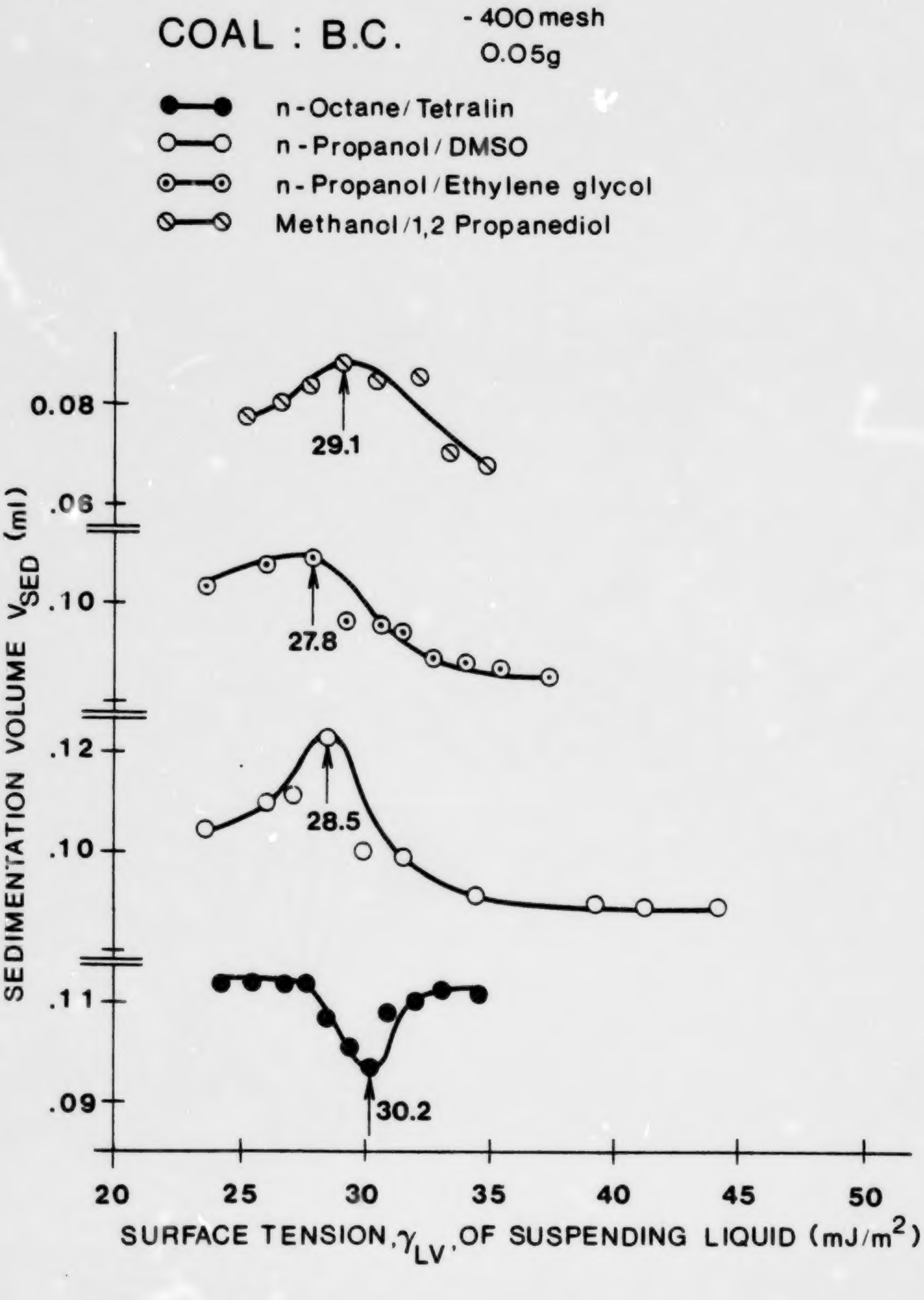

COAL : B.C.
- 400 mesh
0.05g
n-Octane/Tetralin
n-Propanol/DMSO
n-Propanol/Ethylene glycol
Methanol/1,2 Propanediol
29.1
27.8
28.5
30.2
0.08
.06
.10
.12
.10
.11
.09
SEDIMENTATION VOLUME V_SED (ml)
20
25
30
35
40
45
50
SURFACE TENSION, γ_LV, OF SUSPENDING LIQUID (mJ/m²)

Figure 3

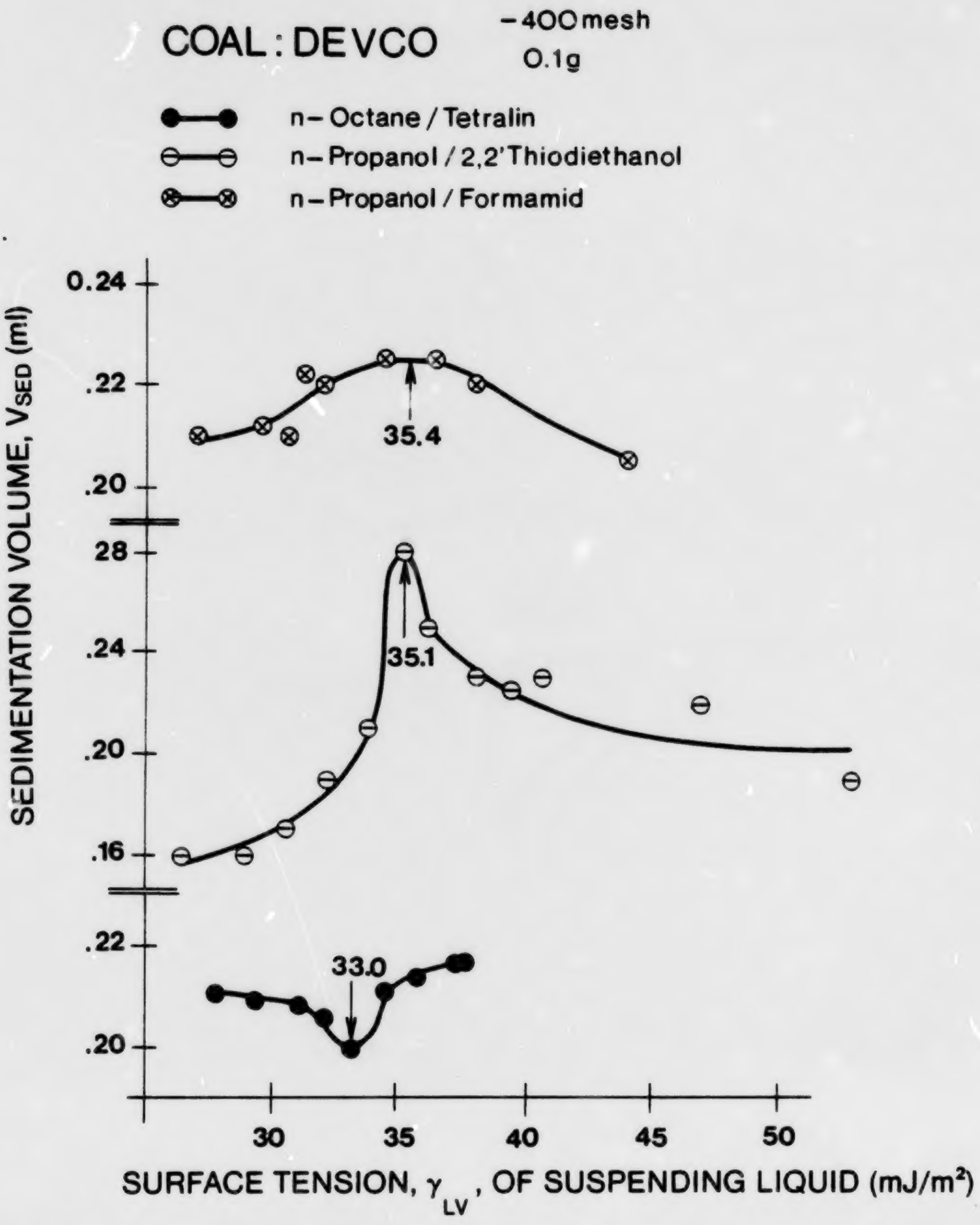

COAL: DEVCO
-400 mesh
0.1g
n-Octane / Tetralin
n-Propanol / 2,2'Thiodiethanol
n-Propanol / Formamid
0.24
.22
.20
28
.24
.20
.16
.22
.20
35.4
35.1
33.0
30
35
40
45
50
SEDIMENTATION VOLUME, V_{SED} (ml)
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m^2)

Figure 4

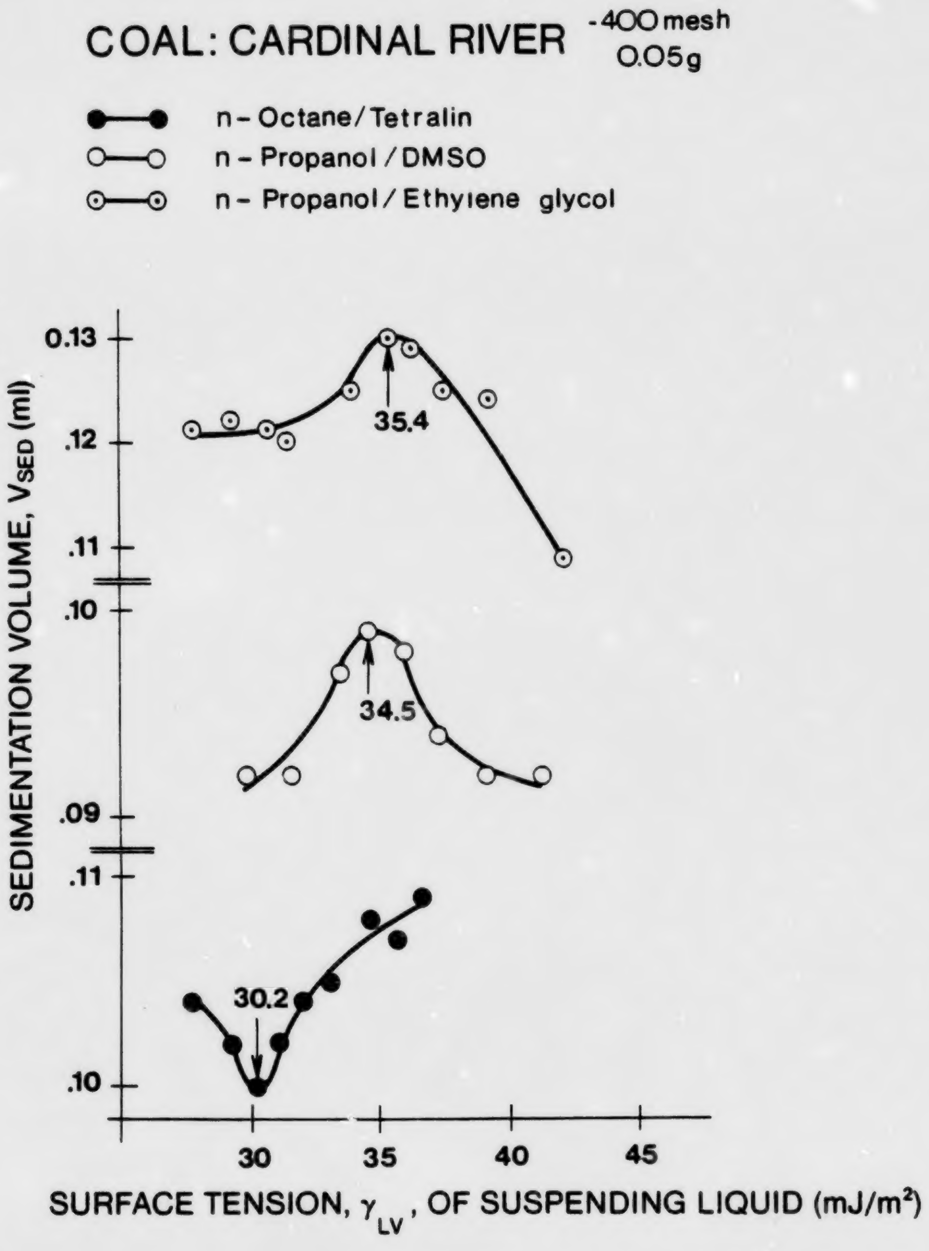

COAL: CARDINAL RIVER -400 mesh 0.05g
n-Octane/Tetralin
n-Propanol/DMSO
n-Propanol/Ethylene glycol
SEDIMENTATION VOLUME, V_{SED} (ml)
0.13
.12
.11
.10
.09
.11
.10
35.4
34.5
30.2
30
35
40
45
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

Figure 5

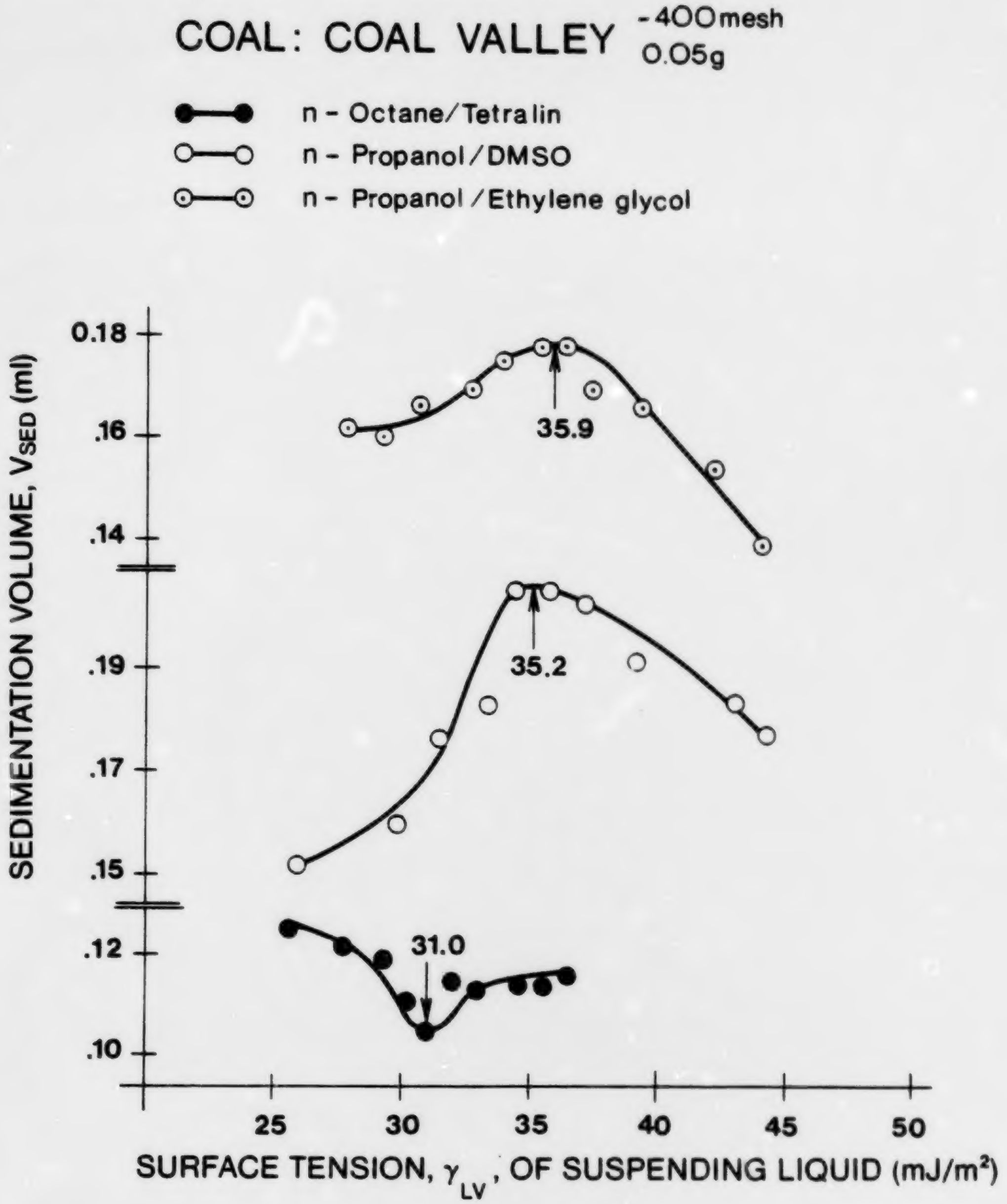

COAL: COAL VALLEY -400mesh 0.05g
n - Octane/Tetralin
n - Propanol/DMSO
n - Propanol/Ethylene glycol
SEDIMENTATION VOLUME, V_{SED} (ml)
0.18
.16
.14
.19
.17
.15
.12
.10
35.9
35.2
31.0
25
30
35
40
45
50
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

Figure 6

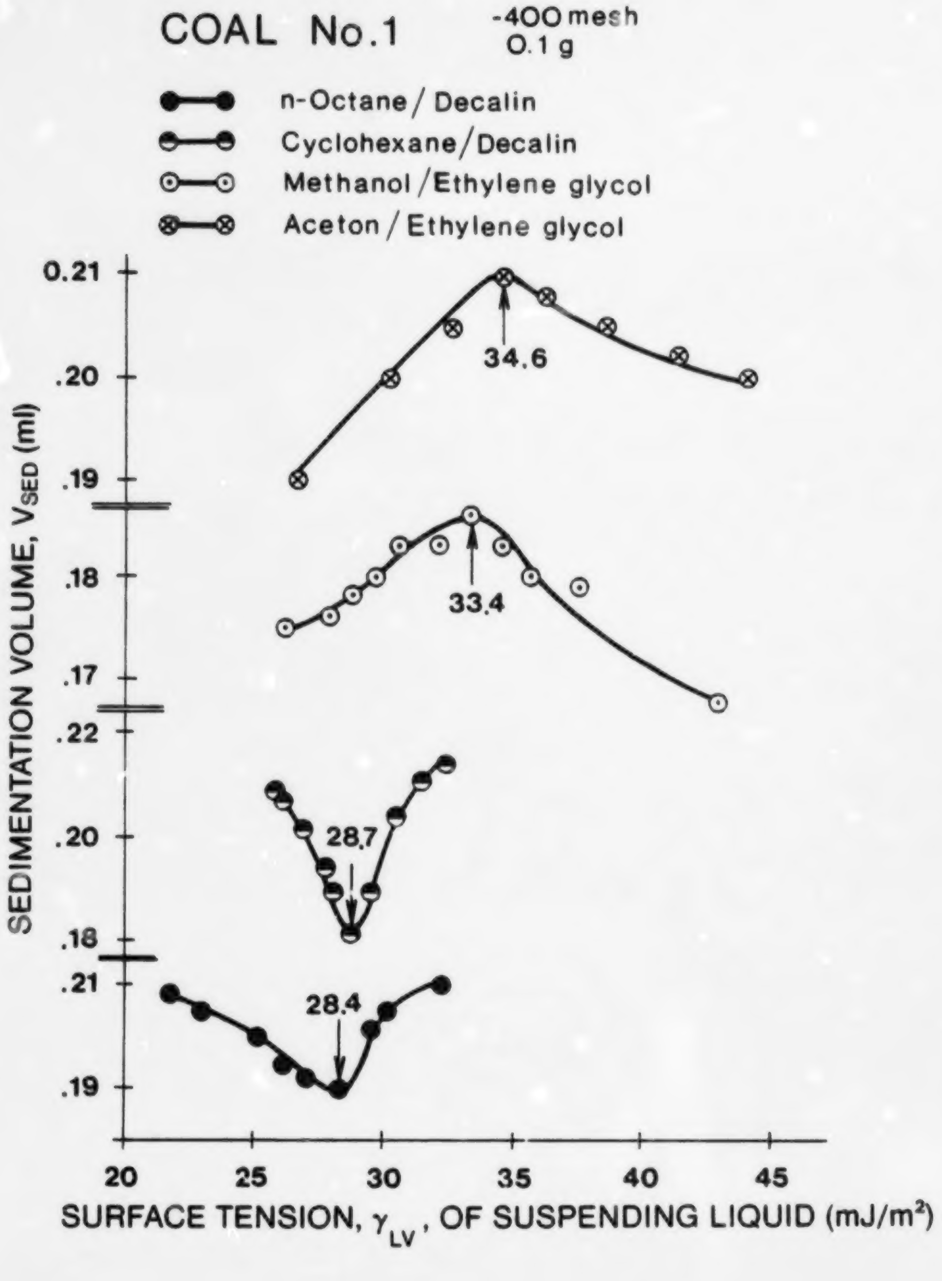

COAL No.1
-400 mesh
0.1 g
n-Octane / Decalin
Cyclohexane / Decalin
Methanol / Ethylene glycol
Aceton / Ethylene glycol
0.21
.20
.19
.18
.17
.22
.20
.18
.21
.19
34.6
33.4
28.7
28.4
SEDIMENTATION VOLUME, V_SED (ml)
20
25
30
35
40
45
SURFACE TENSION, γ_LV, OF SUSPENDING LIQUID (mJ/m²)

Figure 7

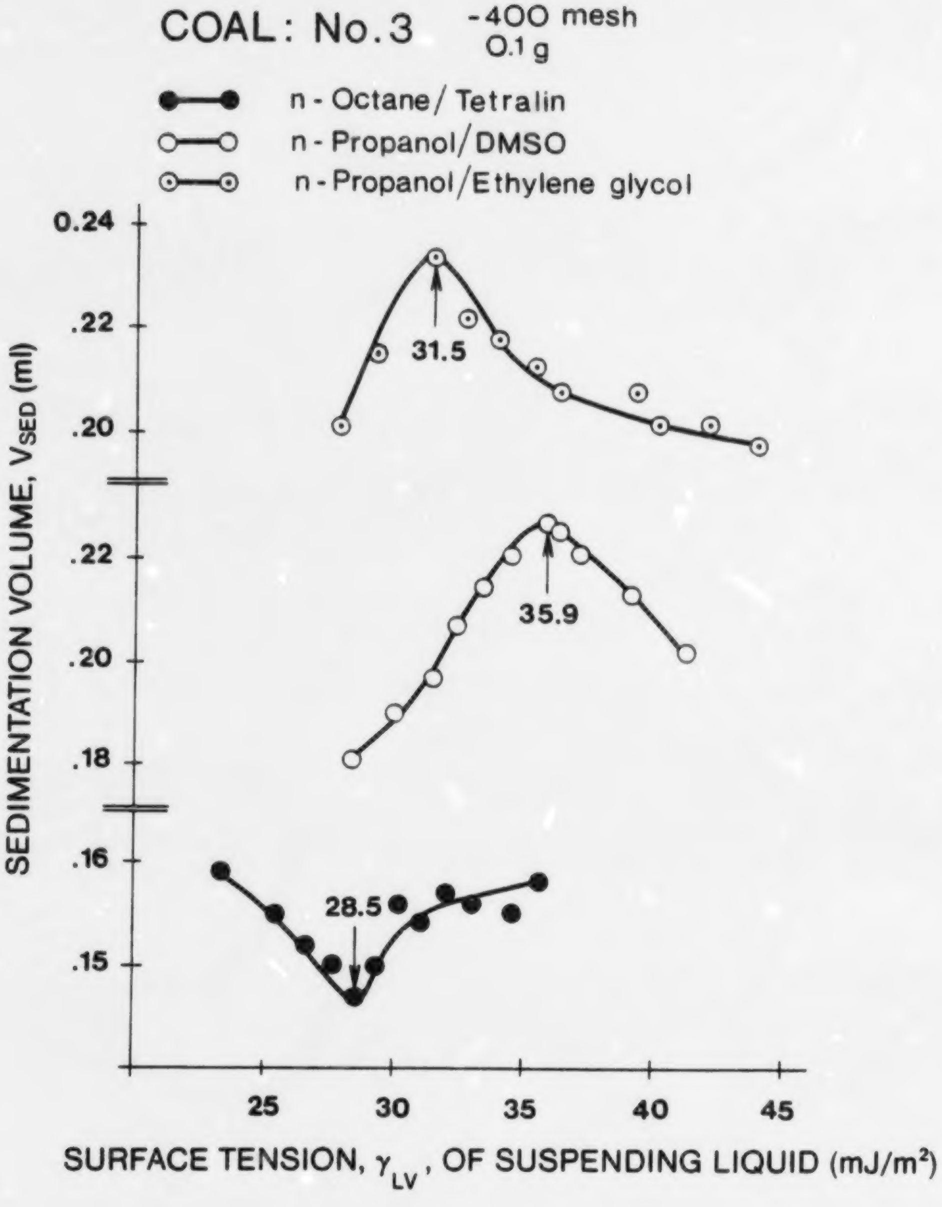

COAL: No.3 -400 mesh 0.1 g
n-Octane/Tetralin
n-Propanol/DMSO
n-Propanol/Ethylene glycol
0.24
.22
.20
.22
.20
.18
.16
.15
31.5
35.9
28.5
SEDIMENTATION VOLUME, V_SED (ml)
25
30
35
40
45
SURFACE TENSION, γ_LV, OF SUSPENDING LIQUID (mJ/m²)

Figure 8

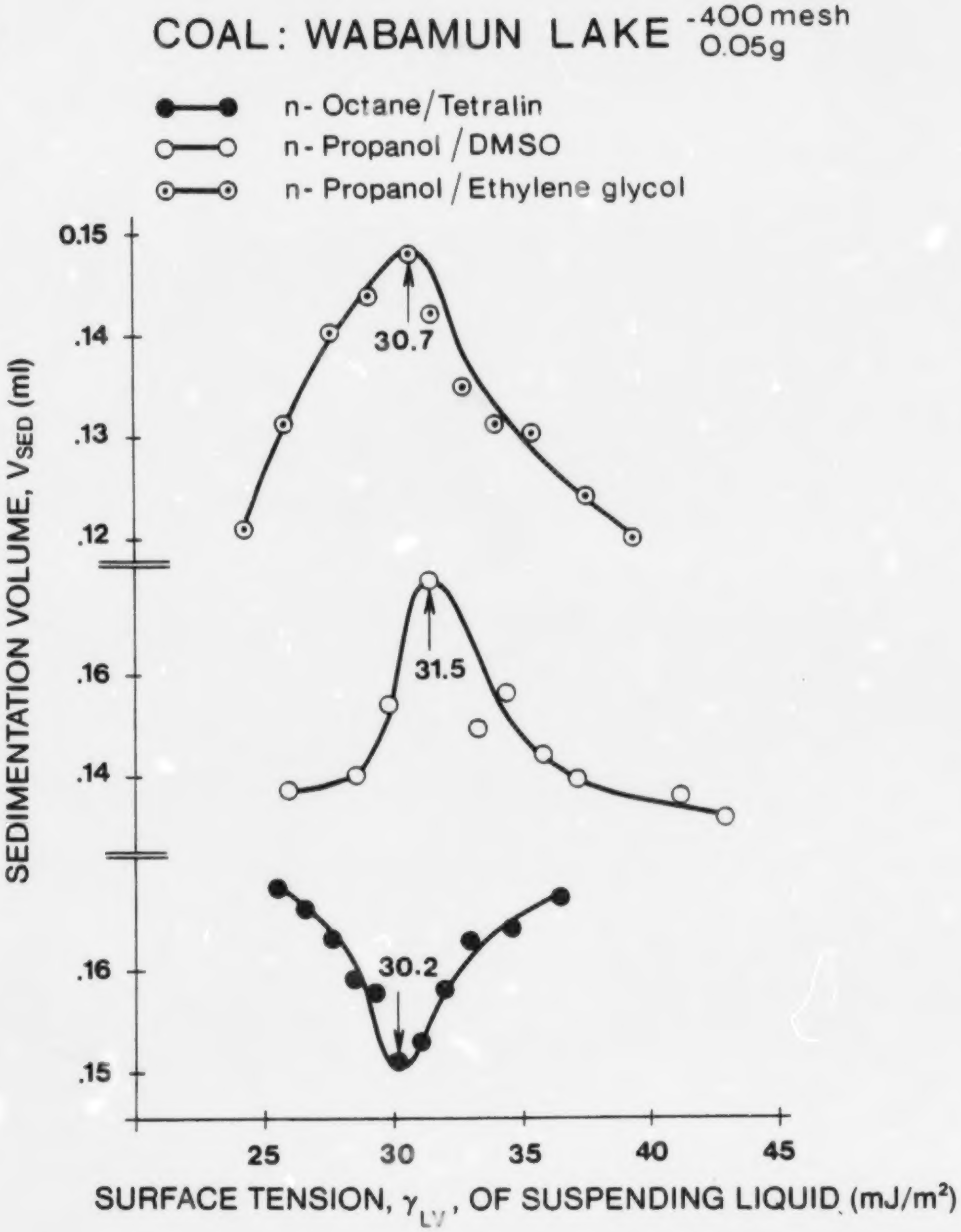

COAL: WABAMUN LAKE -400 mesh 0.05g
n- Octane/Tetralin
n- Propanol / DMSO
n- Propanol / Ethylene glycol
0.15
.14
.13
.12
.16
.14
.16
.15
30.7
31.5
30.2
SEDIMENTATION VOLUME, V_{SED} (ml)
25
30
35
40
45
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

Figure 9

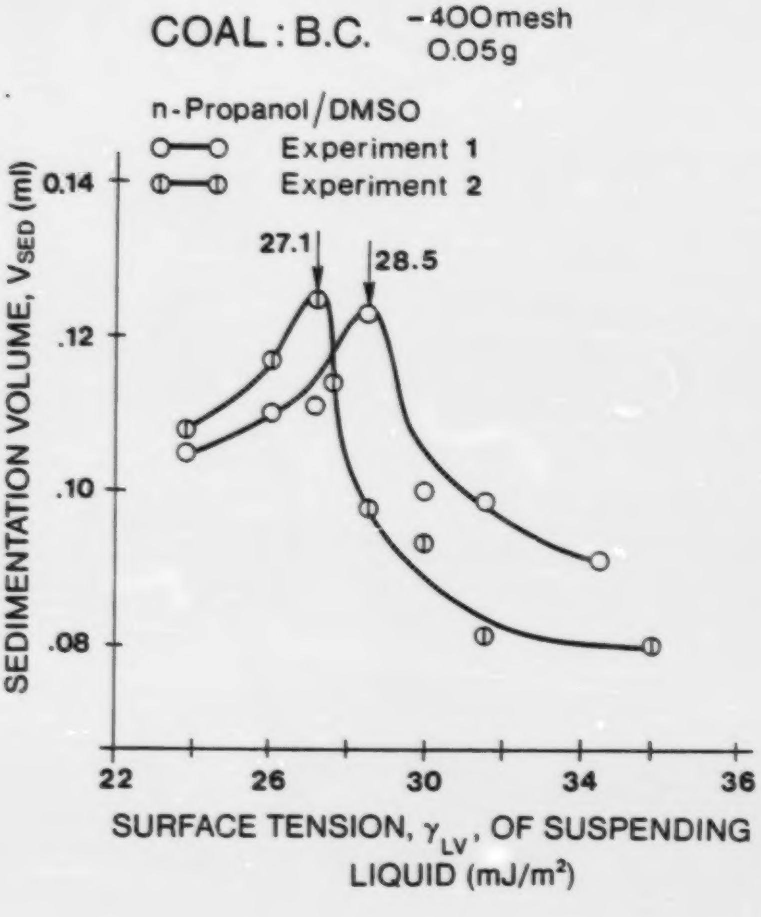

COAL : B.C. -400mesh 0.05g
n-Propanol/DMSO
Experiment 1
Experiment 2
SEDIMENTATION VOLUME, V_{SED} (ml)
0.14
.12
.10
.08
27.1
28.5
22
26
30
34
36
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m^2)

Figure 10

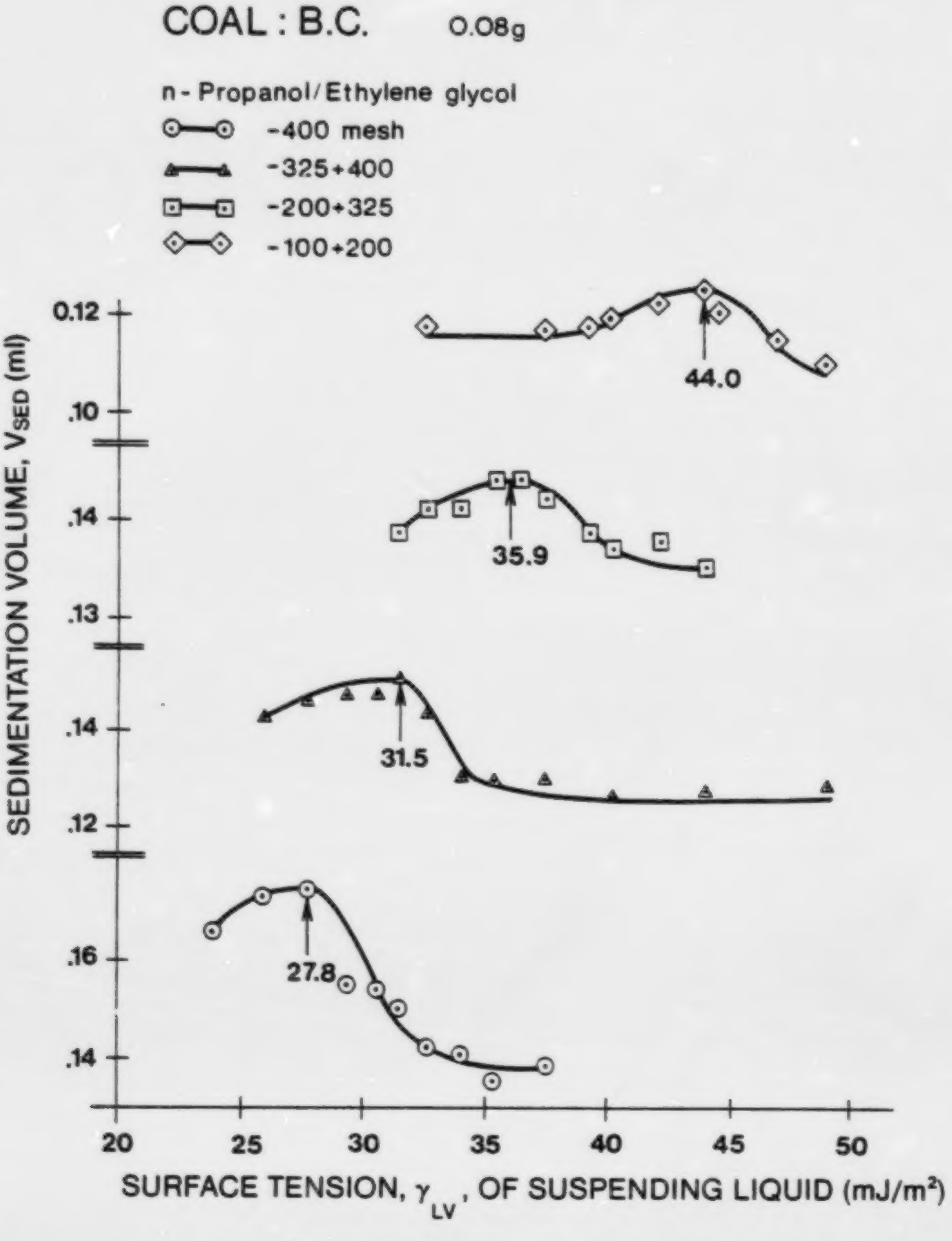

COAL : B.C. 0.08g
n-Propanol/Ethylene glycol
-400 mesh
-325+400
-200+325
-100+200
0.12
.10
.14
.13
.14
.12
.16
.14
SEDIMENTATION VOLUME, V_SED (ml)
44.0
35.9
31.5
27.8
20
25
30
35
40
45
50
SURFACE TENSION, γLV, OF SUSPENDING LIQUID (mJ/m²)

Figure 11

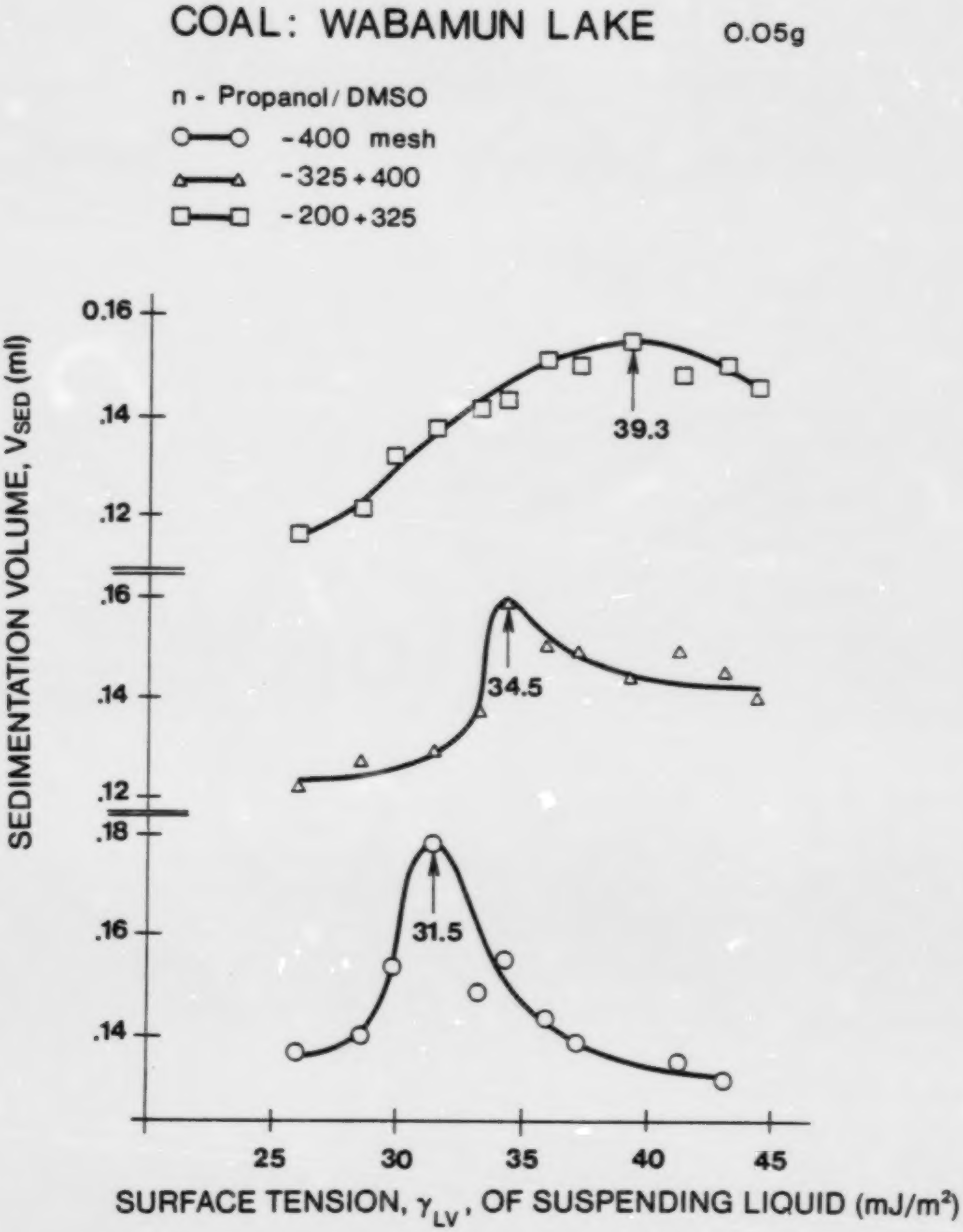

COAL: WABAMUN LAKE 0.05g
n - Propanol / DMSO
-400 mesh
-325 + 400
-200 + 325
SEDIMENTATION VOLUME, V_{SED} (ml)
0.16
.14
.12
.16
.14
.12
.18
.16
.14
39.3
34.5
31.5
25
30
35
40
45
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

Figure 12

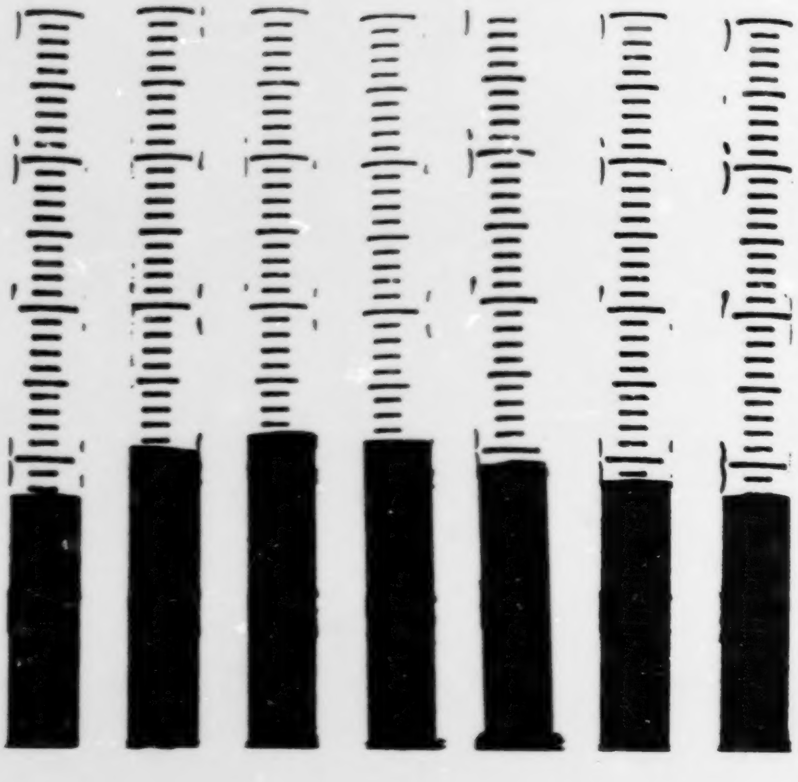


Figure 13

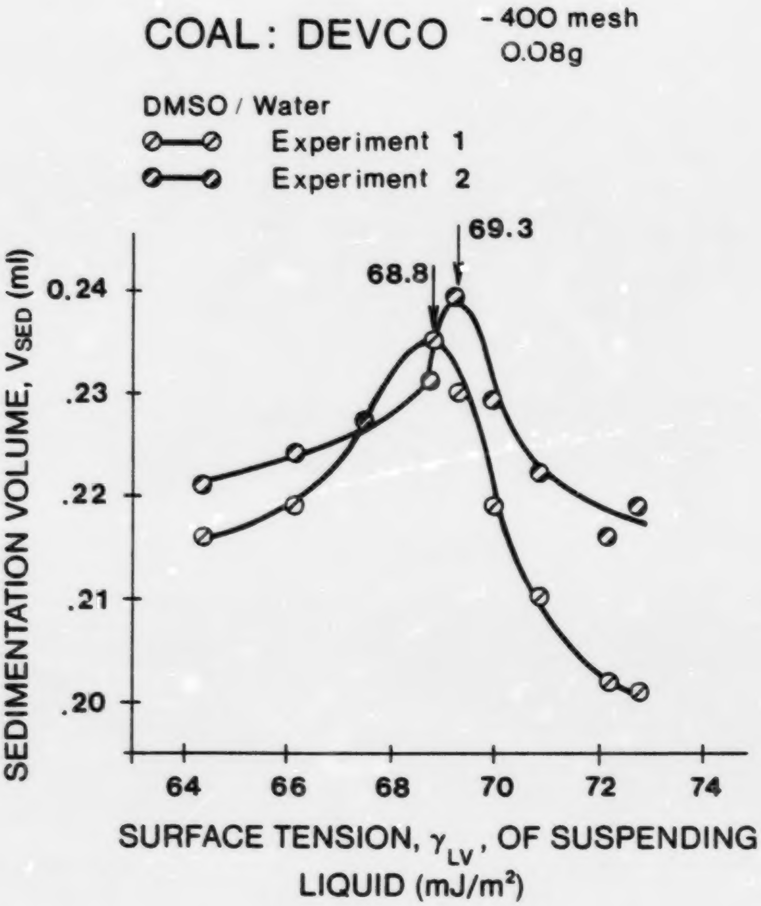

COAL: DEVCO -400 mesh 0.08g
DMSO / Water
Experiment 1
Experiment 2
69.3
68.8
SEDIMENTATION VOLUME, V_{SED} (ml)
0.24
.23
.22
.21
.20
64
66
68
70
72
74
SURFACE TENSION, γ_{LV}, OF SUSPENDING LIQUID (mJ/m²)

Figure 14

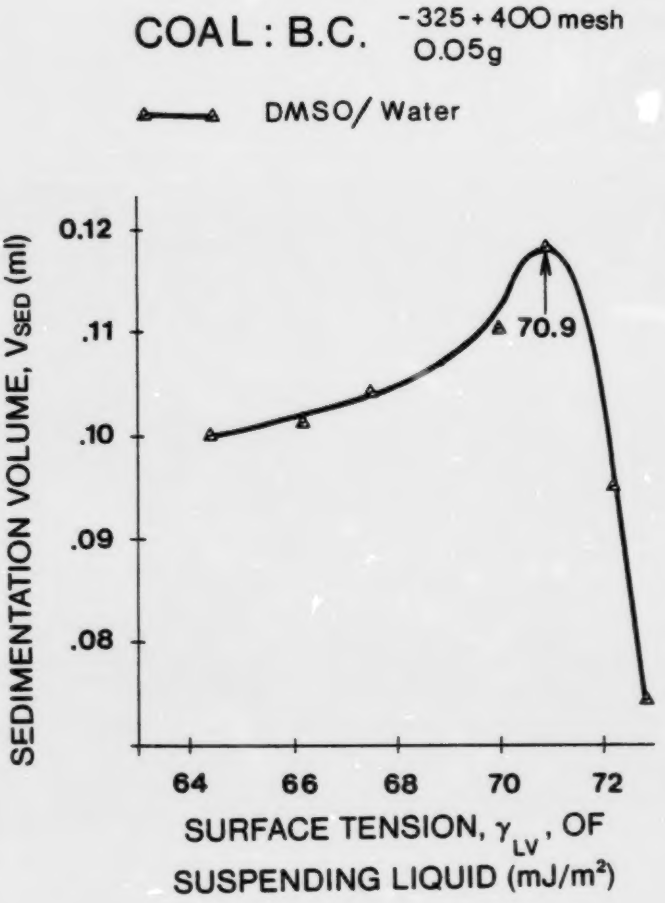
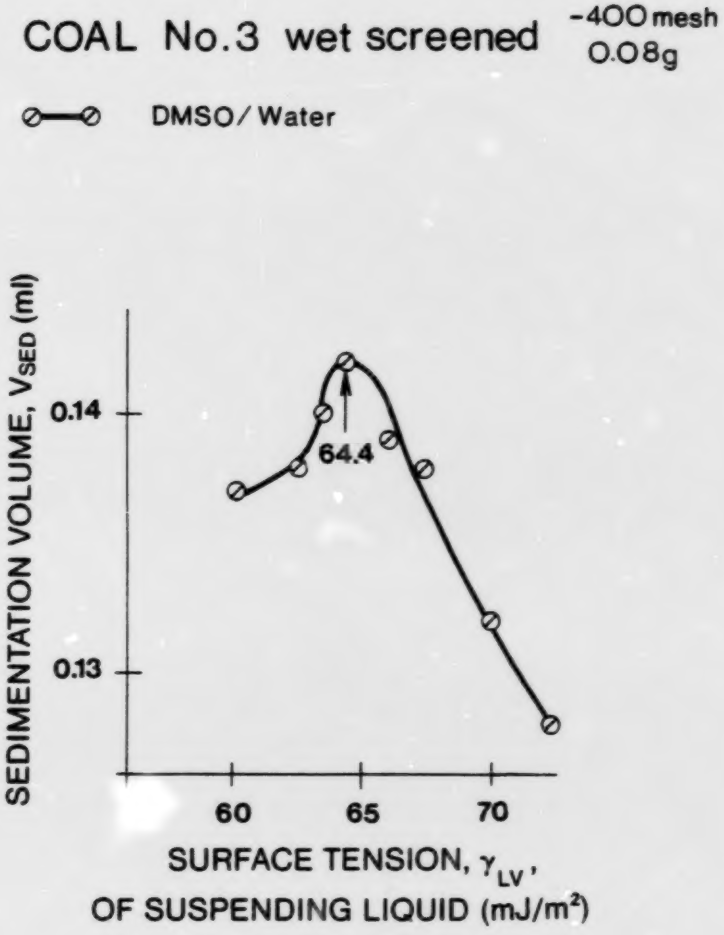

COAL : B.C. -325 + 400 mesh 0.05g
DMSO/ Water
SEDIMENTATION VOLUME, V_SED (ml)
0.12
.11
.10
.09
.08
70.9
64
66
68
70
72
SURFACE TENSION, γ_LV, OF SUSPENDING LIQUID (mJ/m²)

Figure 15



COAL No.3 wet screened -400 mesh 0.08g
DMSO/ Water
SEDIMENTATION VOLUME, V_{SED} (ml)
0.14
0.13
64.4
60
65
70
SURFACE TENSION, γ_{LV},
OF SUSPENDING LIQUID (mJ/m^2)

Figure 16

APPENDIX A

SOLIDIFICATION FRONT EXPERIMENTS FOR COAL SAMPLES IN AN ORGANIC MEDIUM

Coal samples from Western Canada were studied in an organic medium by means of the solidification front technique. The origin, rank, date of mining, type of sizing and the density of the coal samples are given in Table 1. The results of the proximate analysis of some of the coals are summarized in Table 2.

The particle surface tension, γ_{PV}, of B.C., Cardinal River, Coal Valley, Denison and Wabamun Lake coal samples (-60+100, -200+325 and -400 mesh sizes) was determined by measuring the critical velocity of engulfment, V_c, in thymol at 51.5°C. The results are summarized in Tables 3-7. The solidification front velocity, V, versus particle diameter, D, is plotted in Figures 1-5. The corresponding plots of γ_{PV} versus particle diameter, D, at 51.5°C are presented in Figure 6 for these five coal samples. In the range of the small particle sizes ($D < 100$ μm), the surface tensions of these coals just slightly differ from each other but fractions with larger particles ($D > 200$ μm) exhibit a range of surface characteristics. It is surprising that the subbituminous Wabamun Lake sample has one of the most hydrophobic characters, while that of the bituminous B.C. coal is amongst the most hydrophilic. We observed that the change in the surface tension of B.C. coal with increasing particle size is unusually large. The fine fraction of B.C. coal is significantly more hydrophobic than the coarse fractions.

TABLE 1

Origin, Rank, Type of Sizing and Density of Coal Samples

Coal Sample	Origin	Rank and Date of Mining	Type of Sizing	Density ρ (kg/m^3)
B.C.	Kaiser Resources Harmer Seam Pit 29 South British Columbia	bituminous 1982	dry screened	1410
CARDINAL RIVER	Hinton Alberta	bituminous 1982	dry screened	1320
COAL VALLEY	Mynheer A Seam Coal Valley Alberta	bituminous 1983	dry screened	1445
DENISON	Denison Mines Quintette Area British Columbia	bituminous 1983	dry screened	1430
WABAMUN LAKE	Wabamun Lake Alberta	subbituminous 1983	dry screened	1400

TABLE 2

Proximate Analysis of Coals

Coal Sample	Moisture Content (wt%)	Volatile Matter (wt%)	Ash Content (wt%)	Fixed Carbon (wt%)
B.C.	0.43	21.03*	8.45*	70.52*
CARDINAL RIVER	-	-	-	-
COAL VALLEY	2.89	30.65 31.56*	16.87 17.87*	49.59 50.57*
DENISON	0.27	22.39 22.45*	20.20 20.25*	57.14 57.30*
MINTO	0.76	35.00 35.27*	16.81 16.94*	47.43 47.79*
WABAMUN LAKE	6.87	34.16 36.68*	10.64 11.43*	48.33 51.89*

* The values are dry basis (DB) values.

TABLE 3

Critical Velocity, V_c, Free Energy of Adhesion, ΔF^{adh}, Particle Surface Tension, γ_{PV}, and Contact Angle, θ, Values for B.C. Coal at 51.5°C

Matrix: Thymol

Particle Diameter D (μm)	Critical Velocity V_c (μm/sec)	ΔF^{adh} (mJ/m²)	Surface Tension γ_{PV} (mJ/m²)	Contact Angle θ (degree)
15	11.4±2.7	0.080±0.013	35.7±0.9	73.3±1.7
30	10.3±2.4	0.105±0.017	37.5±1.2	70.2±2.2
45	9.4±2.1	0.119±0.018	38.6±1.3	68.2±2.4
60	8.8±1.9	0.131±0.019	39.4±1.4	66.6±2.6
75	8.3±1.8	0.140±0.021	40.1±1.5	65.4±2.8
90	8.0±1.8	0.150±0.023	40.8±1.7	64.1±3.1
120	7.5±1.8	0.165±0.027	41.9±2.0	62.1±3.6
150	7.5±1.8	0.183±0.030	43.2±2.2	59.7±3.9
180	7.5±1.8	0.200±0.033	44.5±2.4	57.6±4.1
210	7.4±1.8	0.214±0.034	45.4±2.4	55.9±4.2
240	7.4±1.8	0.228±0.036	46.5±2.6	54.1±4.5
270	7.4±1.8	0.242±0.040	47.4±2.9	52.5±5.0
300	7.4±1.8	0.254±0.042	48.4±3.0	50.9±5.3

TABLE 4

Critical Velocity, V_c, Free Energy of Adhesion, ΔF^{adh}, Particle Surface Tension, γ_{PV}, and Contact Angle, θ, Values for CARDINAL RIVER Coal at 51.5°C

Matrix: Thymol

Particle Diameter D (μm)	Critical Velocity V_c (μm/sec)	ΔF^{adh} (mJ/m^2)	Surface Tension γ_{PV} (mJ/m^2)	Contact Angle θ (degree)
15	13.6±4.2	0.092±0.019	36.5±1.4	71.9±2.5
30	11.7±3.6	0.116±0.024	38.3±1.8	68.7±3.2
45	10.3±3.0	0.129±0.026	39.3±1.9	66.9±3.5
60	9.3±2.6	0.138±0.026	39.9±1.9	65.7±3.6
75	8.5±2.3	0.145±0.027	40.4±2.0	64.8±3.6
90	7.9±2.2	0.150±0.029	40.8±2.1	64.0±3.8
120	7.2±2.1	0.162±0.032	41.7±2.4	62.4±4.3
150	6.7±2.0	0.172±0.035	42.4±2.6	61.1±4.6
180	6.2±1.9	0.178±0.037	42.9±2.7	60.3±4.8
210	6.0±1.8	0.188±0.039	43.5±2.8	59.1±4.9
240	5.8±1.7	0.196±0.039	44.1±2.8	58.2±4.9
270	5.6±1.6	0.202±0.040	44.6±2.9	57.3±4.9
300	5.5±1.5	0.210±0.039	45.2±2.8	56.3±4.9

TABLE 5

Critical Velocity, V_c, Free Energy of Adhesion, ΔF^{adh}, Particle Surface Tension, γ_{PV}, and Contact Angle, θ, Values for COAL VALLEY Coal at 51.5°C

Matrix: Thymol

Particle Diameter D (μm)	Critical Velocity V_c (μm/sec)	ΔF^{adh} (mJ/m²)	Surface Tension γ_{PV} (mJ/m²)	Contact Angle θ (degree)
15	8.4±1.1	0.065±0.006	34.6±0.4	75.3±0.7
30	7.9±1.1	0.087±0.008	36.2±0.6	72.5±1.1
45	7.5±1.1	0.102±0.010	37.3±0.7	70.5±1.3
60	7.3±1.1	0.115±0.012	38.2±0.9	68.8±1.6
75	-	-	-	-
90	7.0±1.0	0.136±0.013	39.8±1.0	66.0±1.8
120	7.0±1.0	0.156±0.015	41.3±1.1	63.2±2.1
150	6.9±1.0	0.172±0.017	42.4±1.2	61.1±2.2
180	6.9±1.0	0.188±0.019	43.6±1.4	59.1±2.3
210	6.8±1.0	0.201±0.020	44.5±1.5	57.5±2.5
240	6.7±1.0	0.212±0.022	45.3±1.6	56.1±2.7
270	-	-	-	-
300	-	-	-	-

TABLE 6

Critical Velocity, V_c, Free Energy of Adhesion, ΔF^{adh}, Particle Surface Tension, γ_{PV}, and Contact Angle, θ, Values for DENISON Coal at 51.5°C

Matrix: Thymol

Particle Diameter D (μm)	Critical Velocity V_c (μm/sec)	ΔF^{adh} (mJ/m²)	Surface Tension γ_{PV} (mJ/m²)	Contact Angle θ (degree)
15	-	-	-	-
30	-	-	-	-
45	6.1±1.1	0.089±0.011	36.3±0.8	72.3±1.4
60	5.6±1.0	0.096±0.012	36.9±0.9	71.3±1.5
75	-	-	-	-
90	4.8±1.0	0.105±0.015	37.5±1.1	70.1±2.0
120	4.4±1.0	0.114±0.018	38.2±1.3	68.9±2.3
150	4.1±1.0	0.121±0.020	38.7±1.5	68.0±2.7
180	3.9±1.0	0.128±0.022	39.2±1.6	67.1±3.0
210	3.8±1.0	0.135±0.024	39.7±1.8	66.1±3.3
240	3.7±0.9	0.141±0.024	40.2±1.7	65.2±3.2
270	3.7±0.9	0.150±0.025	40.8±1.8	64.1±3.4
300	3.6±0.8	0.155±0.024	41.1±1.7	63.4±3.2

TABLE 7

Critical Velocity, V_c, Free Energy of Adhesion, ΔF^{adh}, Particle Surface Tension, γ_{PV}, and Contact Angle, θ, Values for WABAMUN LAKE Coal at 51.5°C

Matrix: Thymol

Particle Diameter D (μm)	Critical Velocity V_c (μm/sec)	ΔF^{adh} (mJ/m^2)	Surface Tension γ_{PV} (mJ/m^2)	Contact Angle θ (degree)
15	7.1±1.5	0.058±0.008	34.1±0.6	76.2±1.1
30	6.5±1.4	0.076±0.011	35.4±0.8	73.8±1.4
45	6.1±1.3	0.089±0.013	36.4±0.9	72.2±1.7
60	5.8±1.2	0.099±0.014	37.1±1.0	70.9±1.8
75	-	-	-	-
90	5.4±1.1	0.114±0.016	38.2±1.2	68.9±2.1
120	5.2±1.0	0.128±0.017	39.2±1.2	67.0±2.2
150	5.0±0.9	0.139±0.017	40.0±1.3	65.6±2.3
180	4.9±0.9	0.150±0.019	40.8±1.4	64.1±2.6
210	4.8±0.9	0.159±0.020	41.5±1.5	62.8±2.7
240	4.6±0.8	0.165±0.020	41.9±1.4	62.0±2.6
270	4.4±0.4	0.169±0.021	42.2±1.5	61.4±2.8
300	-	-	-	-

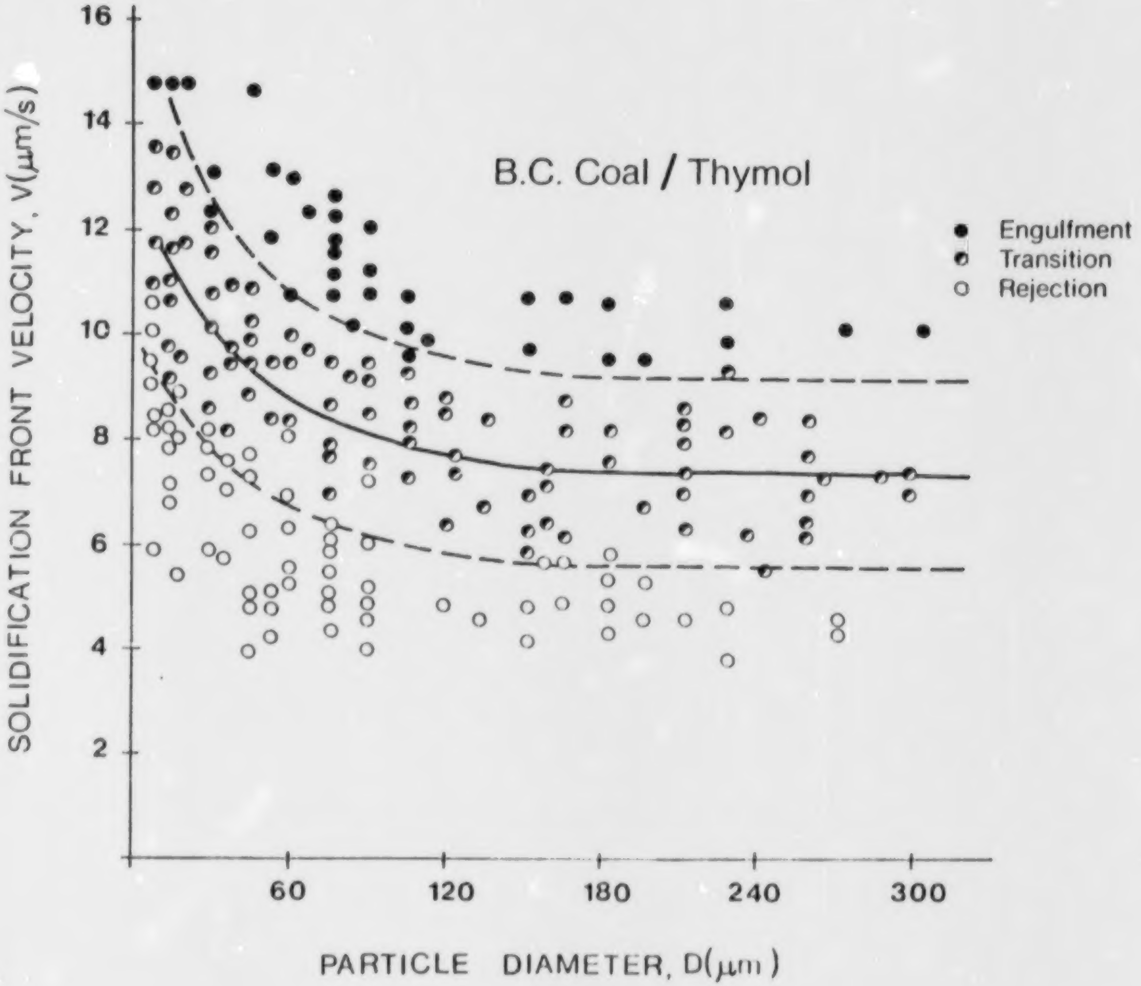


Figure 1: Solidification Front Velocity, V, versus Particle Diameter, D, for B.C. Coal

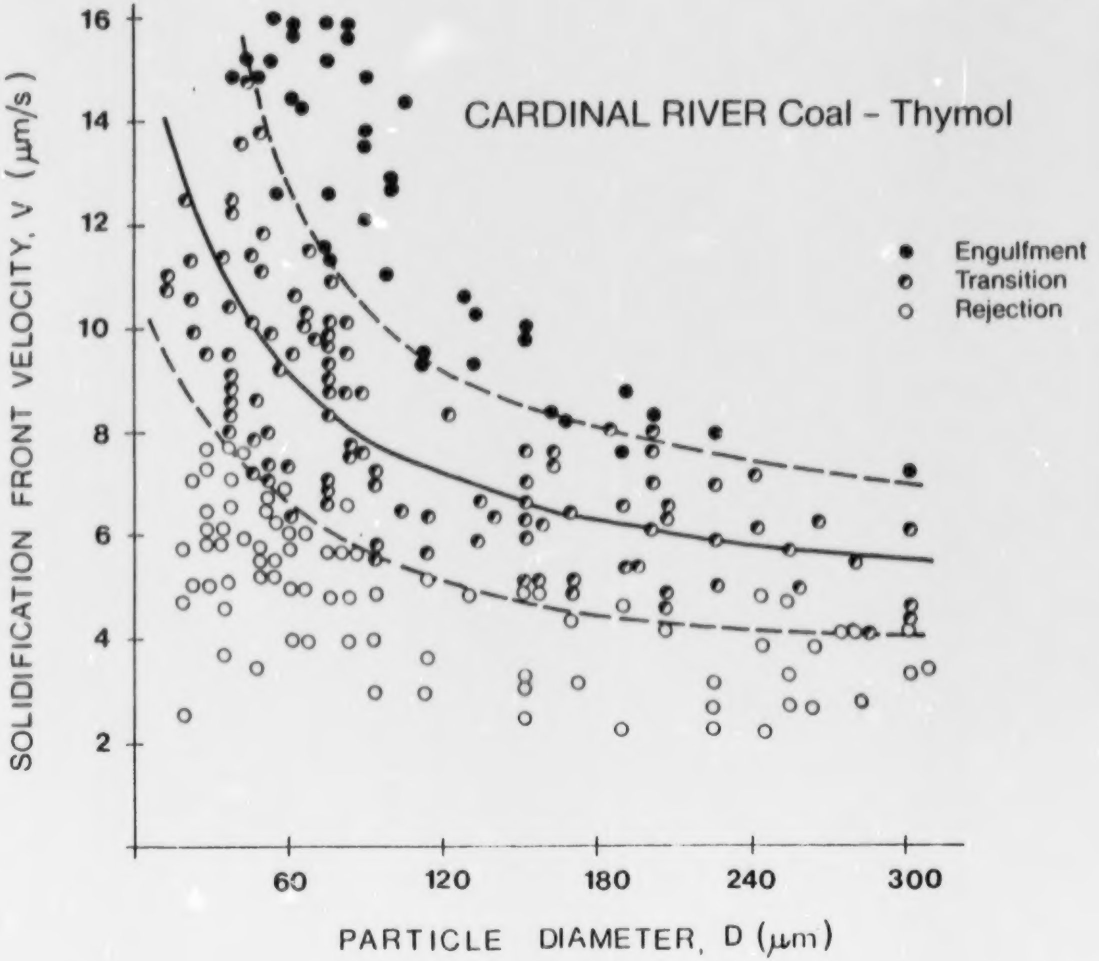


Figure 2: Solidification Front Velocity, V, versus Particle Diameter, D, for Cardinal River Coal

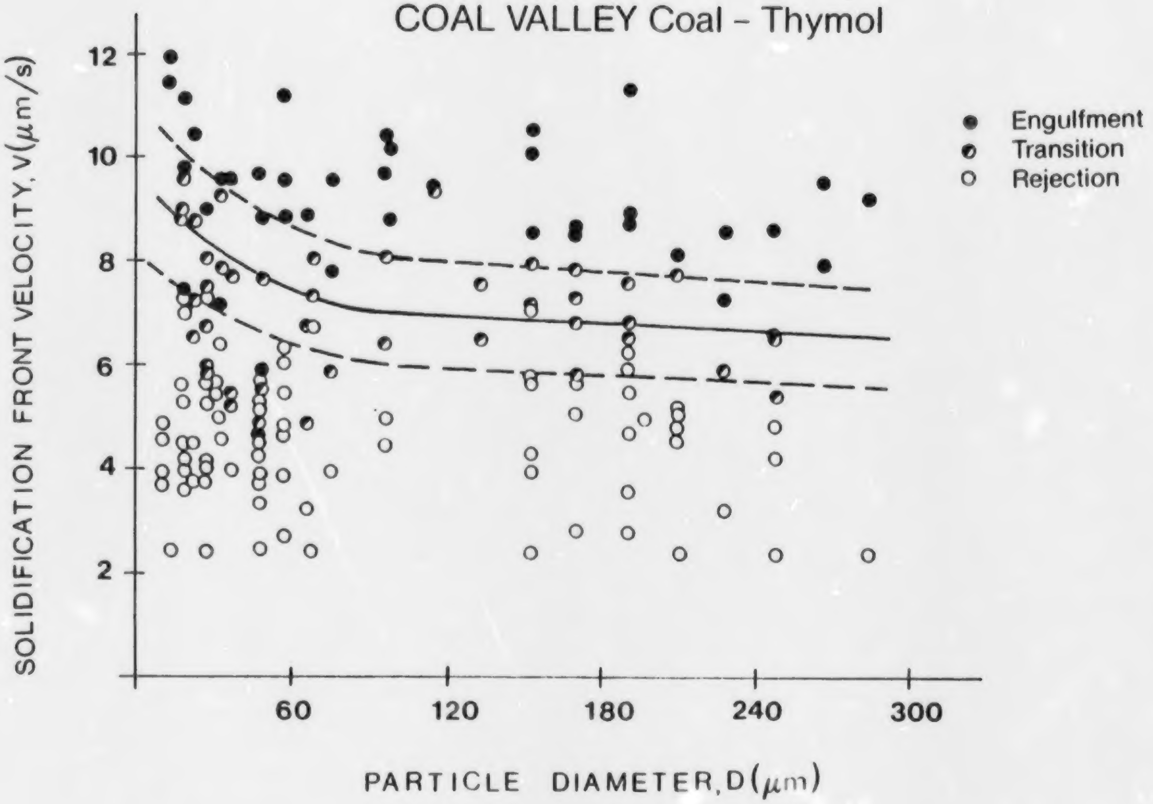


Figure 3: Solidification Front Velocity, V, versus Particle Diameter, D, for Coal Valley Coal

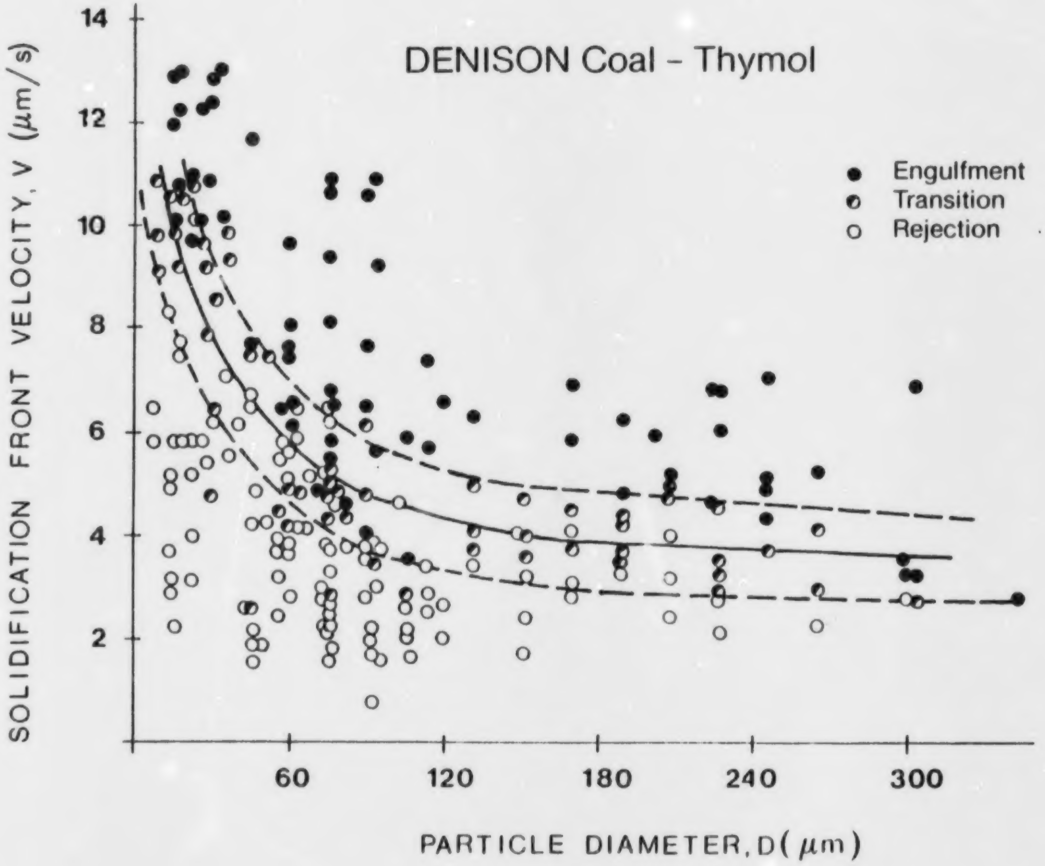


Figure 4: Solidification Front Velocity, V, versus Particle Diameter, D, for Denison Coal

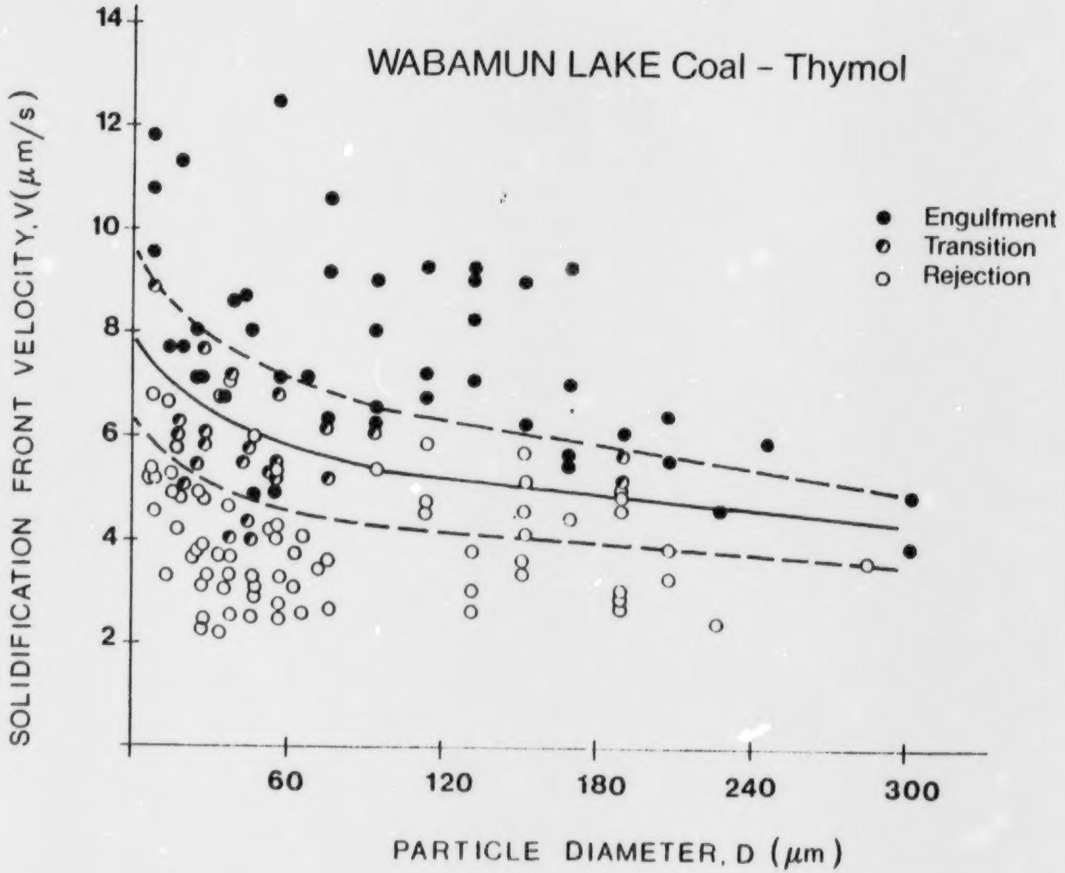


Figure 5: Solidification Front Velocity, V, versus Particle Diameter, D, for Wabamun Lake Coal

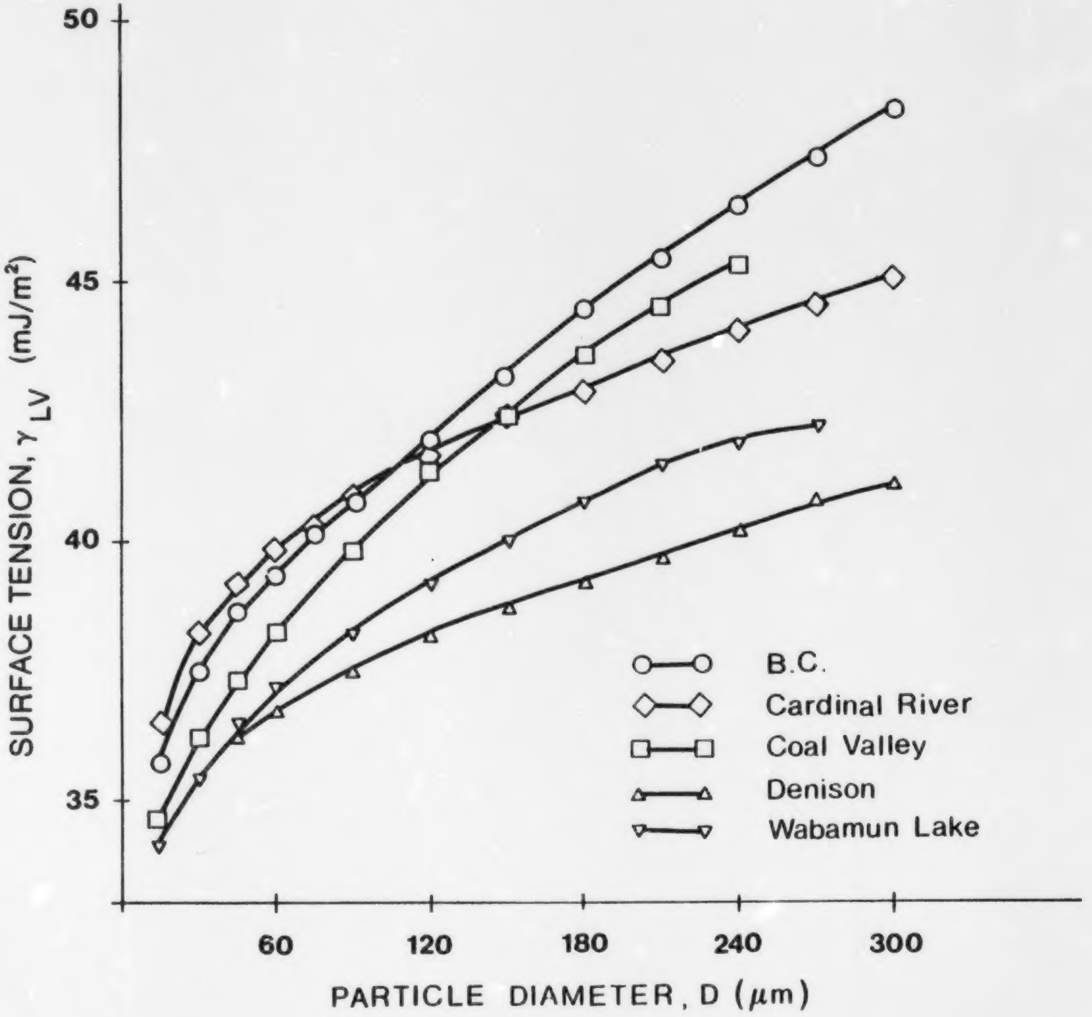


Figure 6: Particle Surface Tension, γ_{PV}, as a Function of Particle Diameter, D, for Various Coal Samples at 51.5°C

APPENDIX B

SUPPLEMENTARY SEDIMENTATION VOLUME, V_{sed}, MEASUREMENTS FOR COAL SAMPLES

The results summarized in Study No. IV do not comprise all of the work done with coal powders by means of the sedimentation technique. Therefore, the previously unreported results obtained for Minto (-400 mesh), Denison (-325+400 mesh) and Wabamun Lake (-325+400 mesh) coal fractions are given in Table 8. The relevant sedimentation volumes, V_{sed}, are plotted in Figures 7-9 as a function of the surface tensions, γ_{LV}, of the suspending liquids. It is worth mentioning that we obtained, for Minto coal, a maximum at γ_{LV} = 39.9 mJ/m^2 in the aqueous solution of n-propanol, a value near to that surface tension obtained in the organic polar mixtures of n-propanol/2,2' thiodiethanol (maximum at γ_{LV} = 38.0 mJ/m^2). However, this experiment was not extended to the higher water concentrations and thus higher γ_{LV} range, hence the surface tensions of the suspending liquids used for sedimentation were below 50 mJ/m^2. It would be interesting to perform experiments covering a wide range of liquid surface tensions, from 23.8 mJ/m^2 (surface tension of n-propanol) to 72.8 mJ/m^2 (surface tension of water at 20°C), to study whether the hydrophobic as well as the hydrophilic behaviour of the coal surface can be shown in the same liquid combination by varying the ratio of the organic and aqueous components.

TABLE 8

Extrema of Sedimentation Volumes, V_{sed}, for MINTO, DENISON and WABAMUN LAKE Coal Samples

Coal Sample	MINTO -400 mesh		DENISON -325 +400 mesh		WABAMUN LAKE -325 +400 mesh	
Liquid Pairs Used for Sedimentation	V_{sed} Extremum at γ_{LV} of Liquids					
	Type	γ_{LV} (mJ/m^2)	Type	γ_{LV} (mJ/m^2)	Type	γ_{LV} (mJ/m^2)
n-Octane/Tetralin	min	31.0	min	32.0	min	32.5
n-Propanol/Thiodiethanol	max	38.0	-	-	-	-
n-Propanol/Ethylene glycol	-	-	max	39.3	max	35.4
n-Propanol/DMSO	-	-	-	-	max	34.5
n-Propanol/Water	max	39.9	-	-	-	-

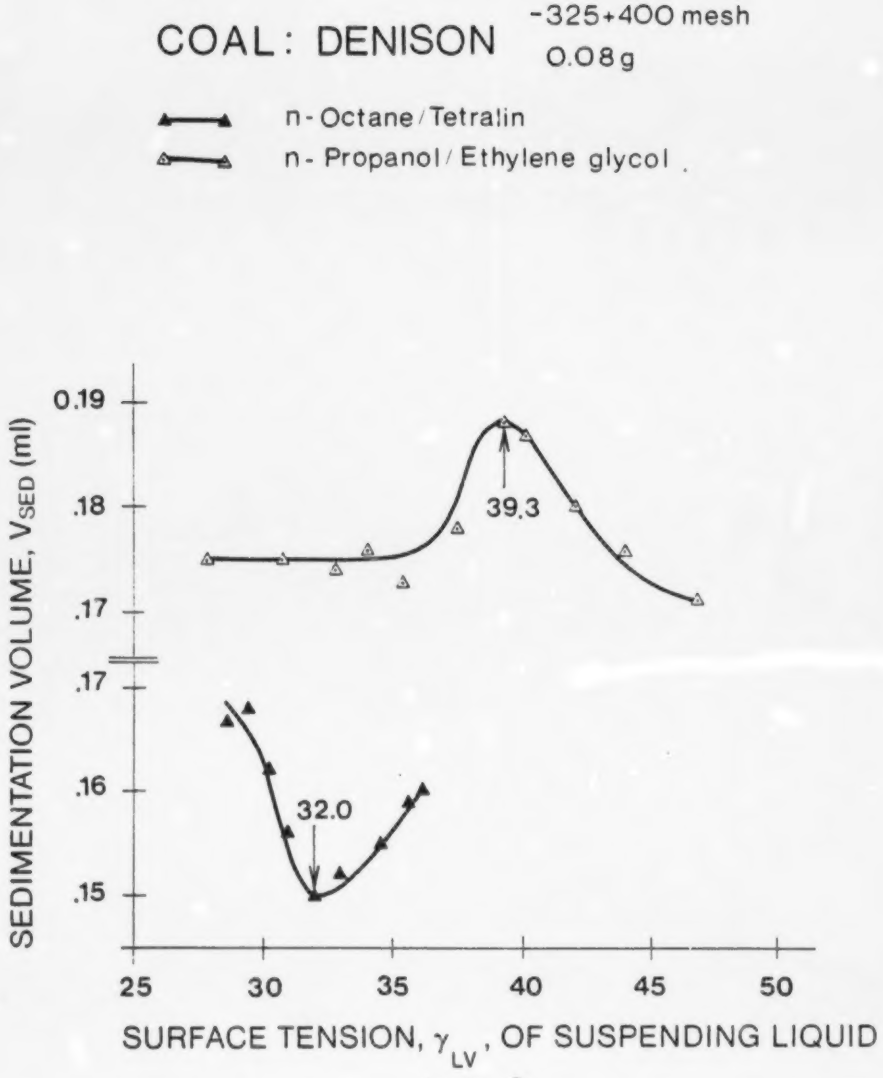


Figure 7: Sedimentation Volume, V_{sed}, as a Function of the Surface Tension, γ_{LV}, of the Suspending Liquid for Denison Coal

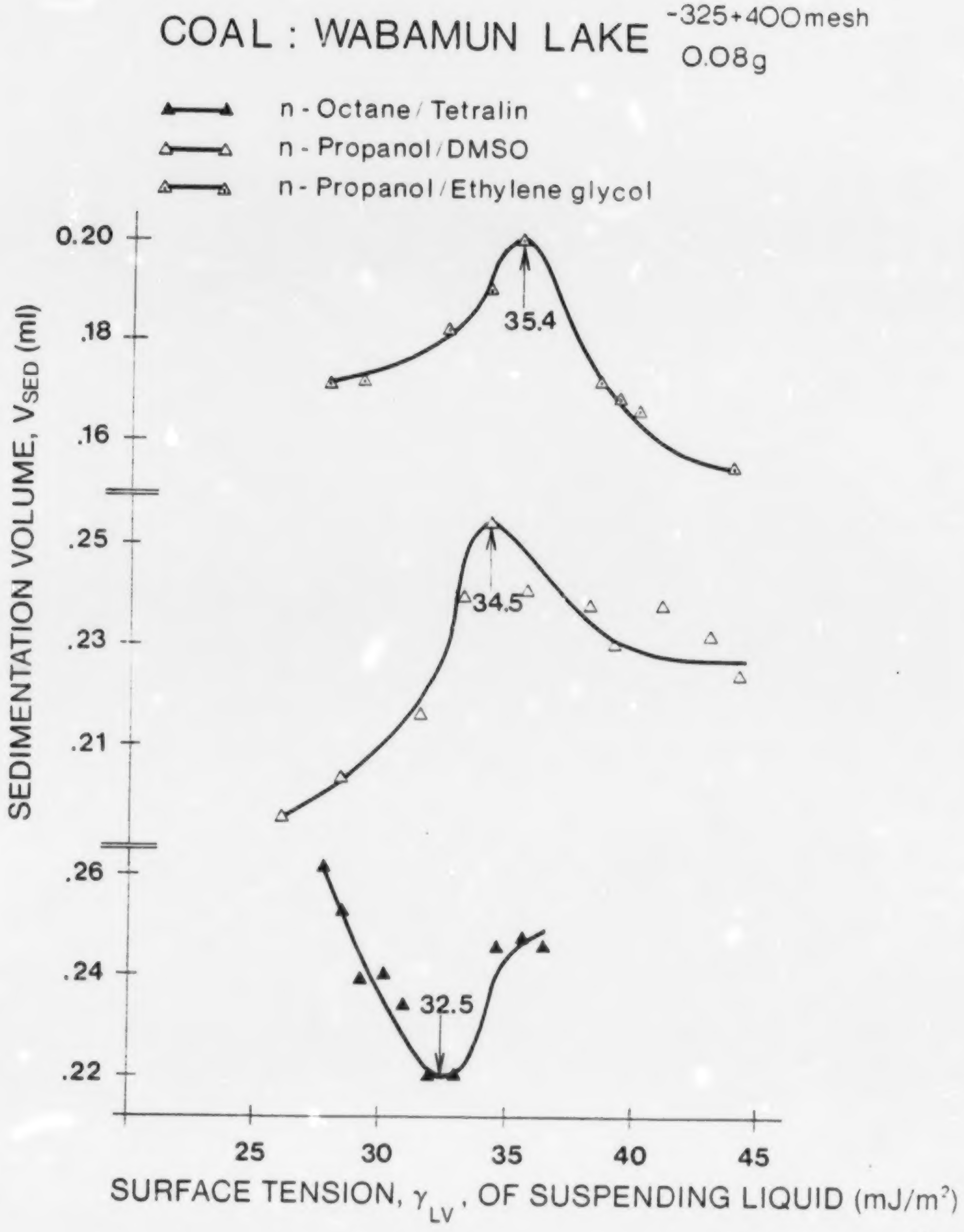


Figure 8: Sedimentation Volume, V_{sed}, as a Function of the Surface Tension, γ_{LV}, of the Suspending Liquid for Wabamun Lake Coal

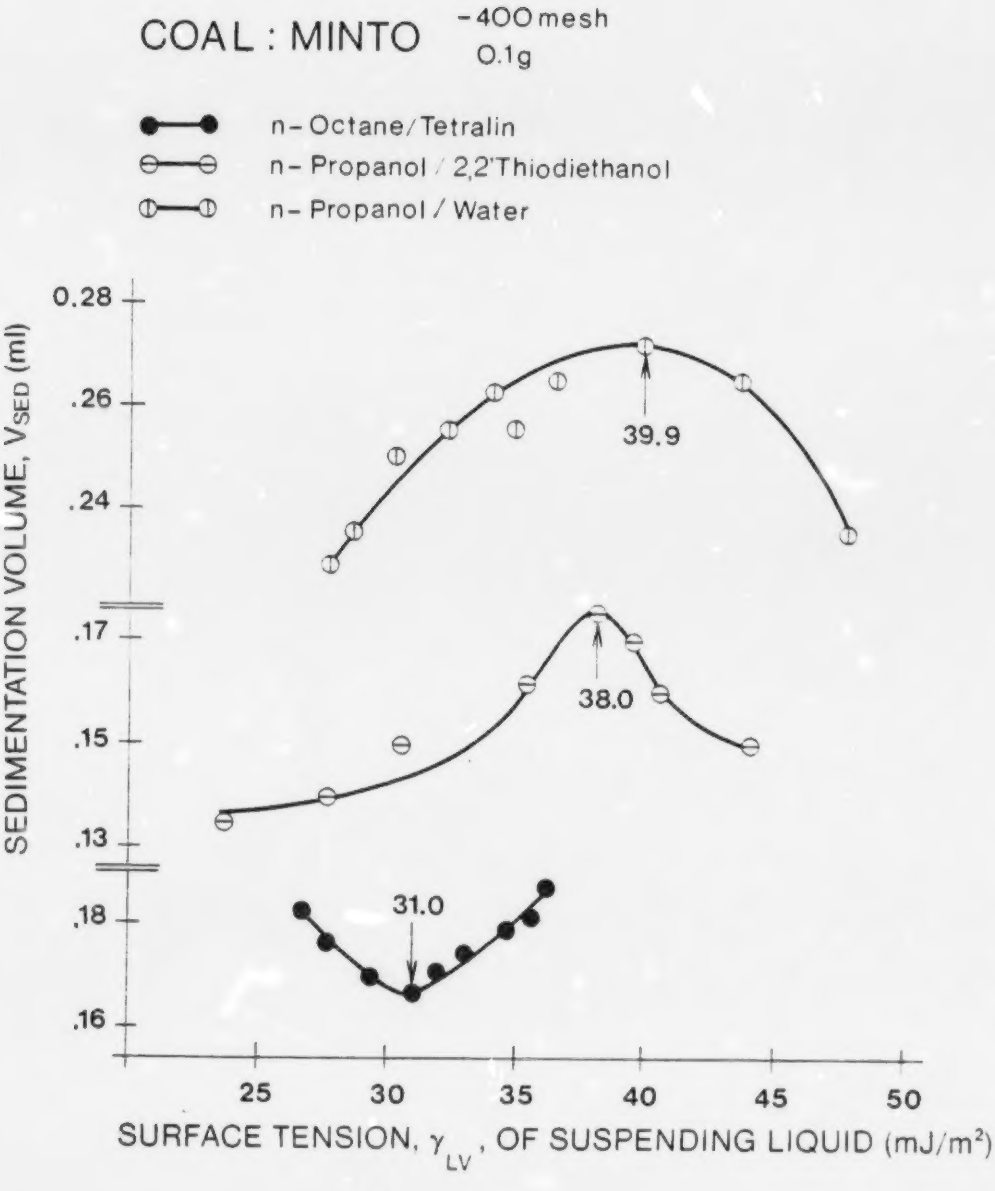


Figure 9: Sedimentation Volume, V_{sed}, as a Function of the Surface Tension, γ_{LV}, of the Suspending Liquid for Minto Coal

APPENDIX C

DETERMINATION OF THE SURFACE TENSION, γ_{LV}, OF PURE LIQUIDS AND BINARY LIQUID MIXTURES

Prior to the sedimentation and adhesion experiments, the surface tension, γ_{LV}, of all of the liquids and liquid mixtures used for those measurements was determined by means of the Wilhelmy plate technique at 20°C. A Cahn electrobalance was used to measure the mass of liquid which was lifted by the platinum plate above the horizontal liquid level. This mass is proportional to the surface tension, γ_{LV}, of the liquid.

The physical properties of twenty-one pure liquids including their surface tensions, densities and dipole moments at 20°C as well as their boiling temperatures are provided in Tables 9/a and 9/b.

The surface tensions, γ_{LV}, of seven liquid pairs in various concentrations are summarized in Tables 10/a and 10/b. The relevant surface tension, γ_{LV}, versus the volumetric percentage of the first liquid component of each liquid pair is plotted in Figures 10-16.

TABLE 9/a

Physical Properties of Liquids

Liquids		Boiling[1] Point b.p. (^{o}C)	Density[1] at 20^{o}C ρ_L (kg/m^3)	Dipole[1] Moment at 20^{o}C $\mu \times 10^{-30}$ (Cm)	Surface Tension at 20^{o}C γ_{LV} (mJ/m^2)	
					Literature[2]	Measured
n-Hexane	C_6H_{14}	68.95	660.3	0	18.40	18.3
n-Octane	C_8H_{18}	125.66	702.5	0	21.62	21.8
n-Hexadecane	$C_{16}H_{34}$	286.80	773.3	0	27.47	27.0
Cyclohexane	C_6H_{12}	80.74	778.6	0	25.24	24.9
Benzene	C_6H_6	80.10	878.7	0	28.88	28.9
Decalin (cis)	$C_{10}H_{18}$	195.65	896.5	0	32.18	32.3
Tetralin	$C_{10}H_{12}$	207.57	970.2	1.63[4]	35.60[5]	36.5
Diethyl ether	$C_4H_{10}O$	34.51	713.8	3.84	17.10	17.4
Methanol	CH_4O	64.96	791.4	5.67	22.50	23.5
n-Propanol	C_3H_8O	97.40	803.5	5.60	23.71	23.8
n-Hexanol	$C_6H_{14}O$	157.83[3]	813.6	5.17[5]	26.21	25.2
Chlorobenzene	C_6H_5Cl	132.00	1105.8	5.64	33.59	33.6
1,2,4 Trichlorobenzene	$C_6H_3Cl_3$	213.50	1454.2	?	39.10[6]	39.7

TABLE 9/b

Physical Properties of Liquids cont'd

Liquids		Boiling[1] Point b.p. (^{o}C)	Density[1] at 20^{o}C ρ_L (kg/m^3)	Dipole[1] Moment at 20^{o}C μx10^{-30} (Cm)	Surface Tension at 20^{o}C γ_{LV} (mJ/m^2)	
					Literature[2]	Measured
Ethylene glycol	$C_2H_6O_2$	198.93	1108.8	7.61	48.43	48.9
1,2 Propanediol	$C_3H_8O_2$	189.00	1036.1	7.51	36.80[4]	35.9
Cyclohexanone	$C_6H_{10}O$	155.65	947.8	9.01[4]	35.19	34.3
Acetone	C_3H_6O	56.20	789.9	9.61	23.70[1]	22.6
Formamide	CH_3NO	111^{20}	1133.4	12.44	58.02[5]	59.9
DMSO	C_2H_6SO	189.00	1101.4	13.21	43.54	44.3
2,2' Thiodiethanol	$C_4H_{10}O_2S$	117^{733}	994.0	?	54.00	52.5
Water	H_2O	100.00	998.2	6.24	72.75	72.8

1 Handbook of Chemistry and Physics, 63rd ed., R.C. Weast (Ed.), CRC Press Inc., Boca Raton, Florida, 1982-83.

2 J. Physical and Chemical Reference Data, Vol. 1, No. 3, D.R. Lide (Ed.), ACS-AIP-NBS Publ., Washington, D.C., 1972.

3 Physico-Chemical Constants of Pure Organic Compounds, J. Timmermans, Elsevier, Amsterdam, 1965.

4 Properties of Polymers, 2nd ed., D.W. van Krevelen (Ed.), Elsevier, Amsterdam, 1976.

5 Lange's Handbook of Chemistry, J.A. Dean (Ed.), McGraw-Hill, New York, 1973.

6 Physical Properties of Chemical Compounds, Vol. 1, ACS, Washington, 1955.

TABLE 10/a

Surface Tension, γ_{LV}, of Liquid Pairs at 20°C

Concentration of 1st Component (Vol. %)	γ_{LV} (mJ/m^2) at 20°C			
	n-Hexane n-Hexadecane	n-Hexane Decalin	n-Octane Tetralin	Diethyl ether n-Hexanol
100	18.3	18.3	21.8	17.4
95	-	18.7	-	-
90	18.9	19.4	-	18.0
85	19.2	19.8	-	-
80	19.5	20.4	23.4	19.0
75	20.0	-	-	-
70	20.3	21.2	24.3	19.8
65	-	-	-	20.2
60	21.1	22.3	25.5	20.5
55	-	-	-	21.1
50	22.0	23.2	26.7	21.5
45	-	-	27.1	-
40	-	24.8	27.7	22.4
35	-	25.2	28.5	-
30	23.7	26.0	29.3	-
20	-	27.5	31.0	23.7
15	-	28.2	32.0	-
10	25.9	29.3	33.0	-
7.5	-	29.6	-	-
5	-	30.2	34.6	-
0	27.0	32.3	36.5	25.2

TABLE 10/b

Surface Tension, γ_{LV}, of Liquid Pairs at 20°C

Concentration of 1st Component (Vol. %)	γ_{LV} (mJ/m^2) at 20°C		
	n-Propanol Cyclohexanone	n-Propanol Ethylene glycol	n-Propanol DMSO
100	23.8	23.8	23.8
90	-	-	24.5
80	25.5	26.0	26.0
70	26.1	-	27.1
60	27.0	27.8	28.5
50	27.8	29.3	29.9
45	28.4	-	30.5
40	29.0	30.7	31.5
35	29.6	31.5	32.4
30	30.3	32.7	33.4
25	-	34.0	34.5
20	31.6	35.4	35.9
17.5	-	36.4	36.3
15	-	37.5	37.2
12.5	-	39.3	38.6
10	33.0	40.2	39.2
7.5	-	42.1	39.9
5	-	44.0	41.3
4	-	44.7	-
2	-	46.8	43.1
0	34.3	48.9	44.3

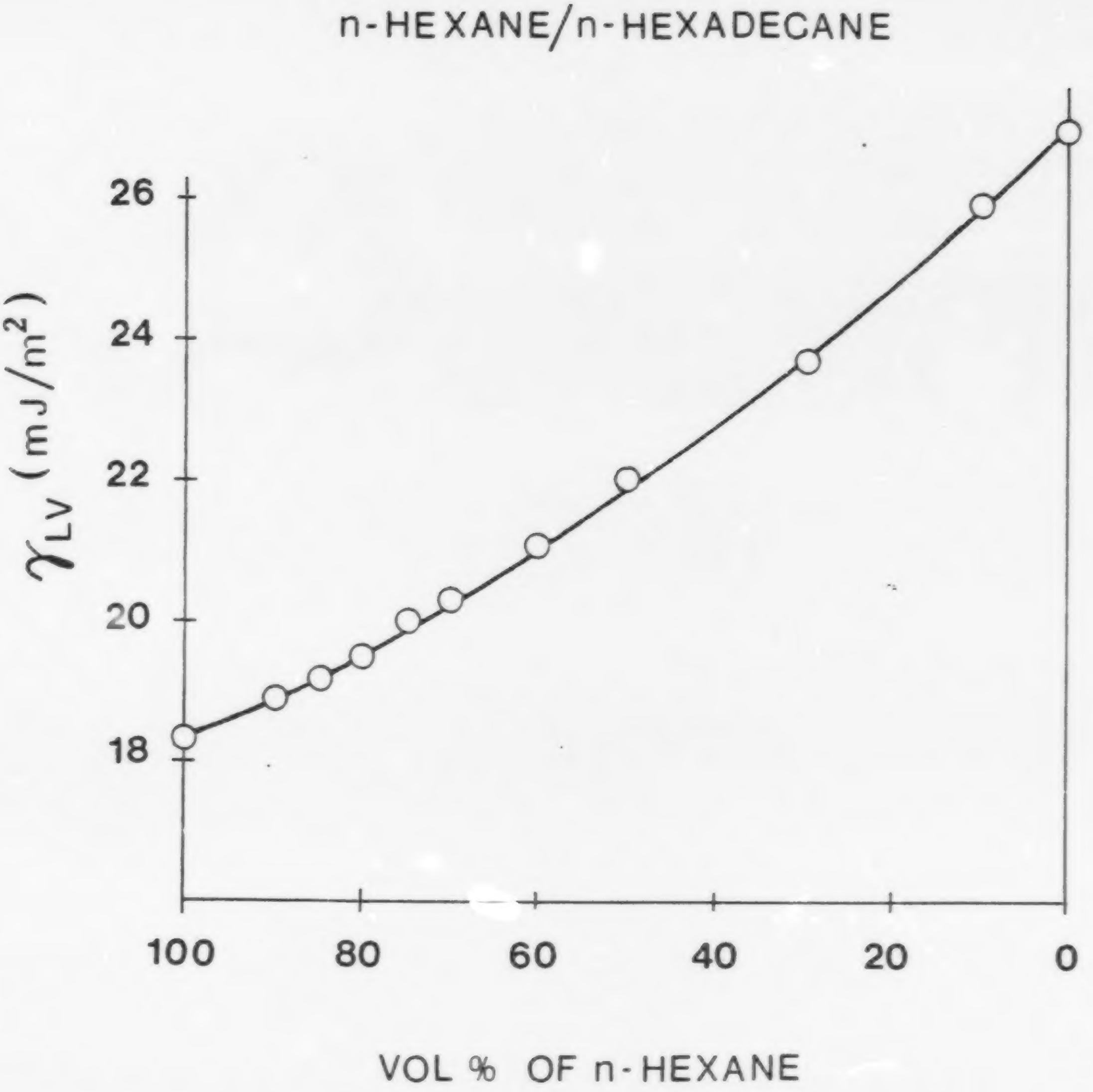


Figure 10: Surface Tension, γ_{LV}, of the Liquid Mixtures of n-Hexane/n-Hexadecane versus Concentration of n-Hexane

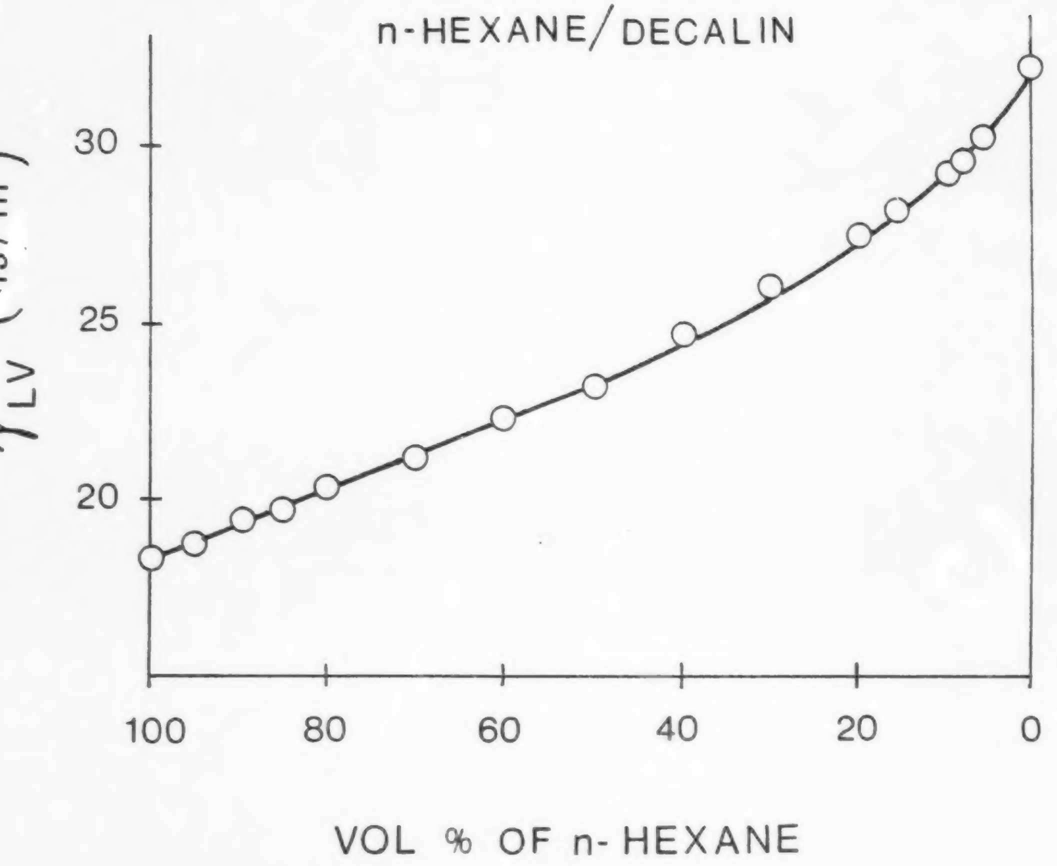


Figure 11: Surface Tension, γ_{LV}, of the Liquid Mixtures of n-Hexane/Decalin versus Concentration of n-Hexane

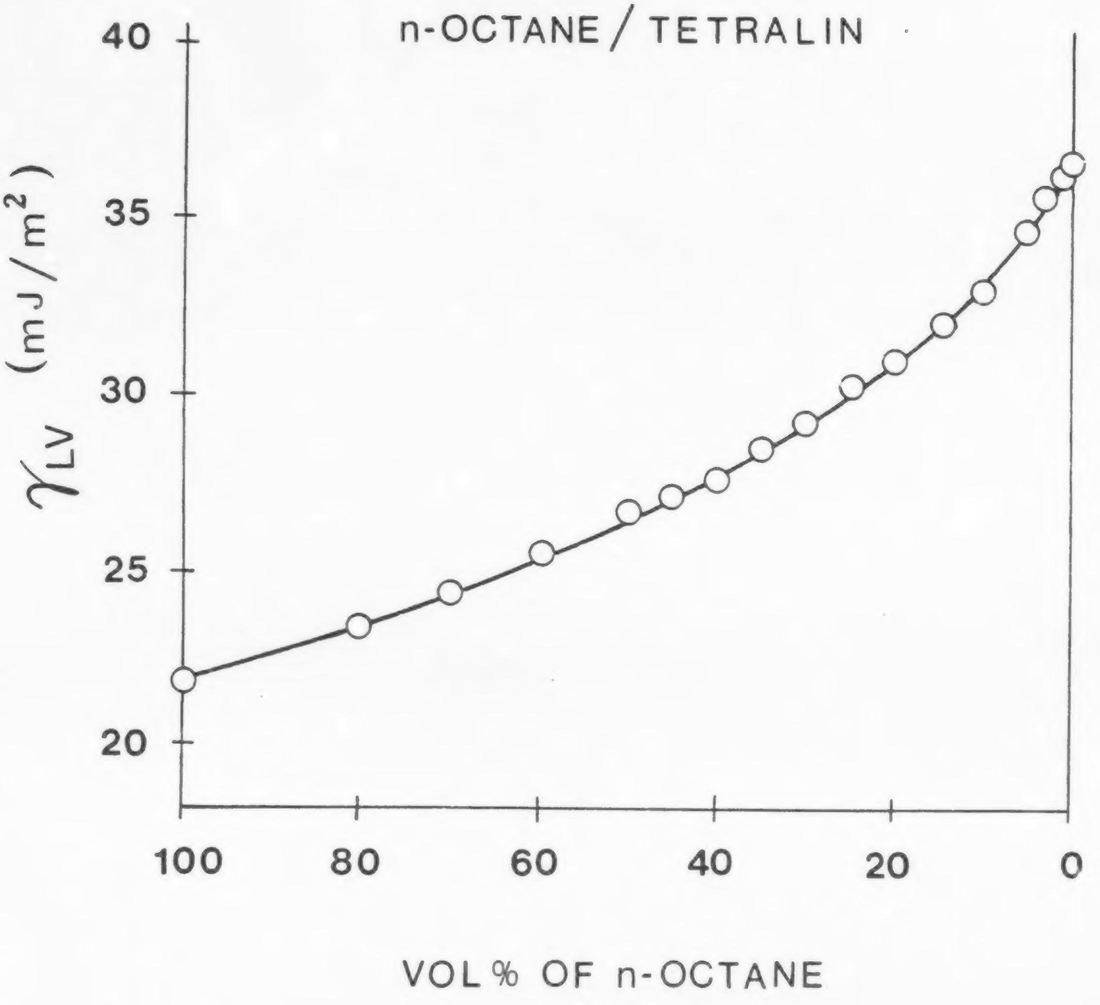


Figure 12: Surface Tension, γ_{LV}, of the Liquid Mixtures of n-Octane/Tetralin versus Concentration of n-Octane

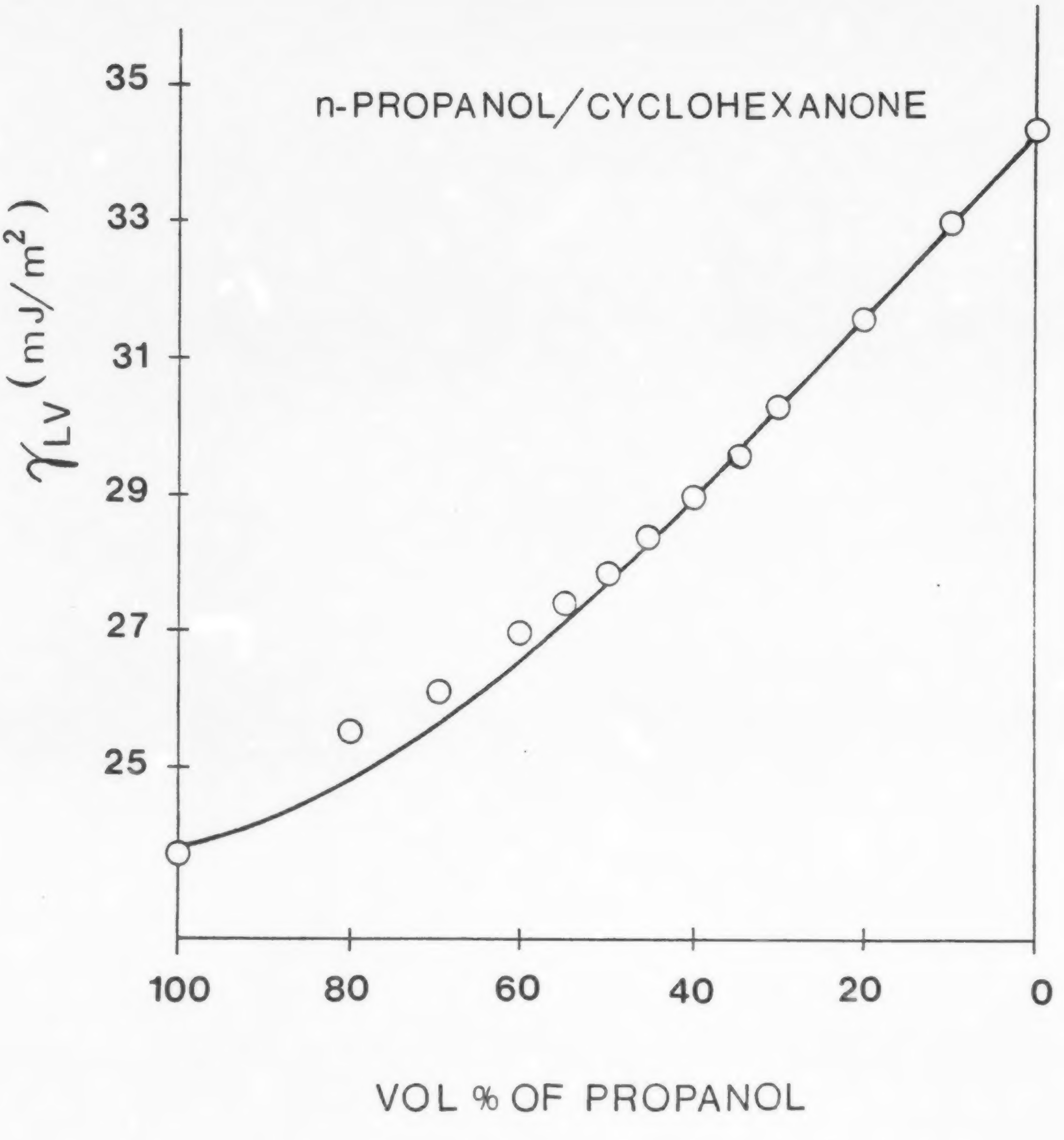


Figure 13: Surface Tension, γ_{LV}, of the Liquid Mixtures of n-Propanol/Cyclohexanone versus Concentration of n-Propanol

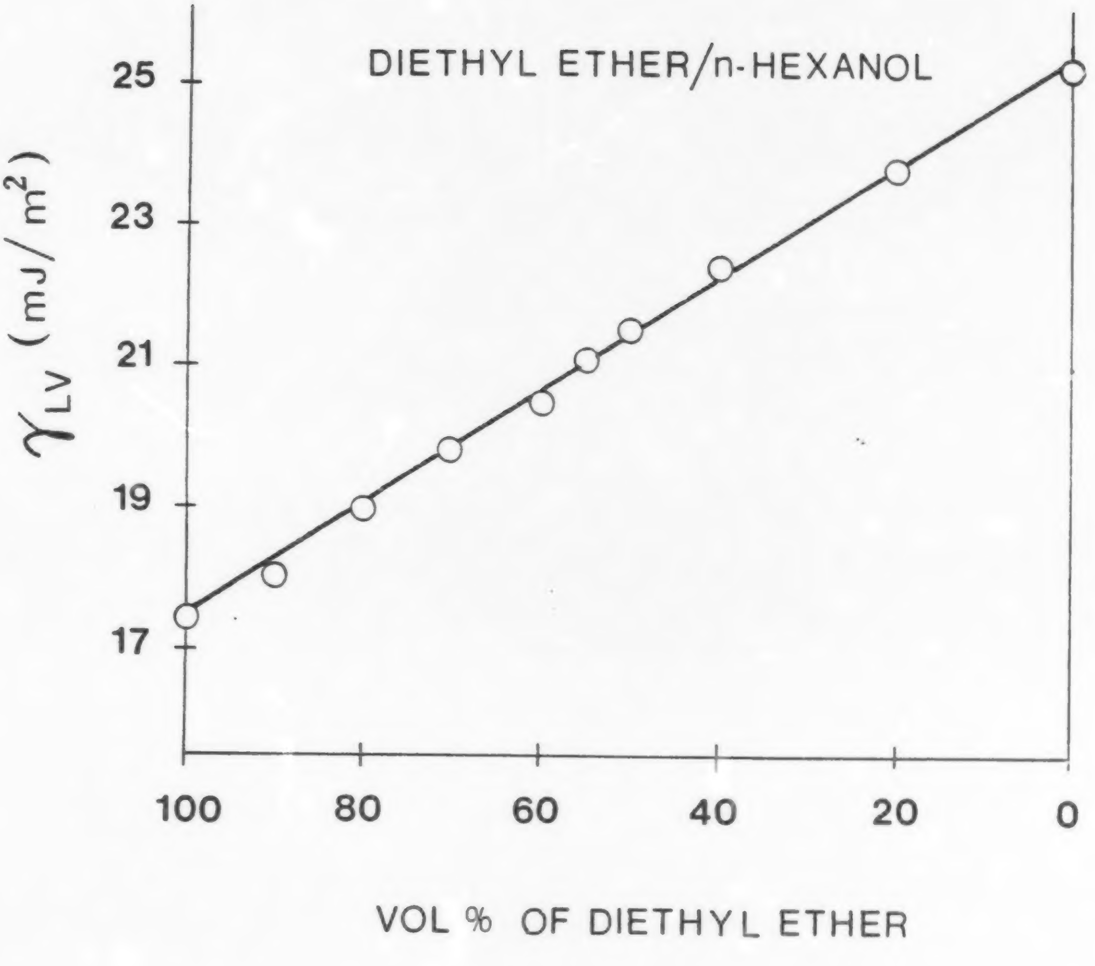


Figure 14: Surface Tension, γ_{LV}, of the Liquid Mixtures of Diethyl ether/n-Hexanol versus Concentration of Diethyl ether

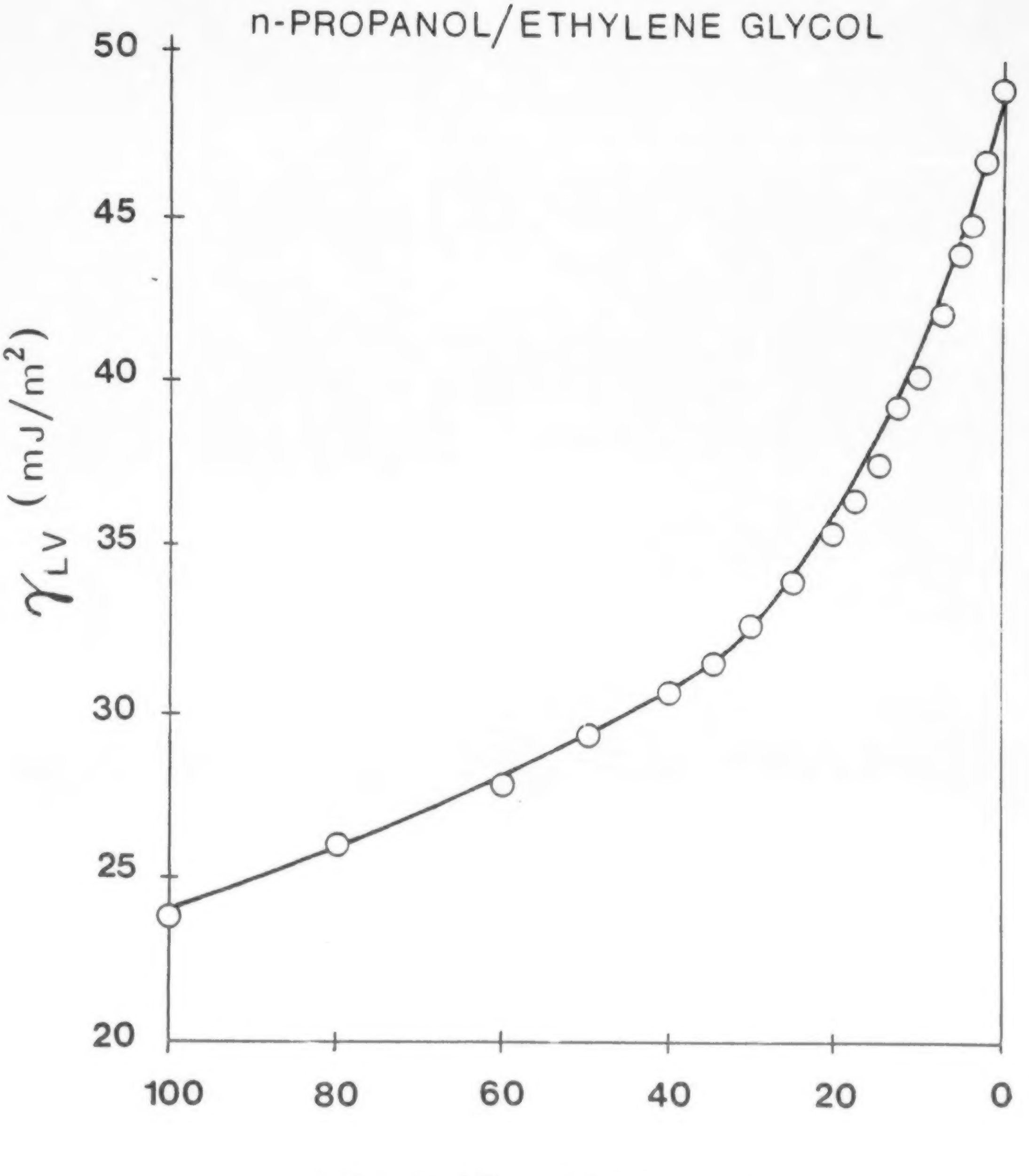


Figure 15: Surface Tension, γ_{LV}, of the Liquid Mixtures of n-Propanol/Ethylene glycol versus Concentration of n-Propanol

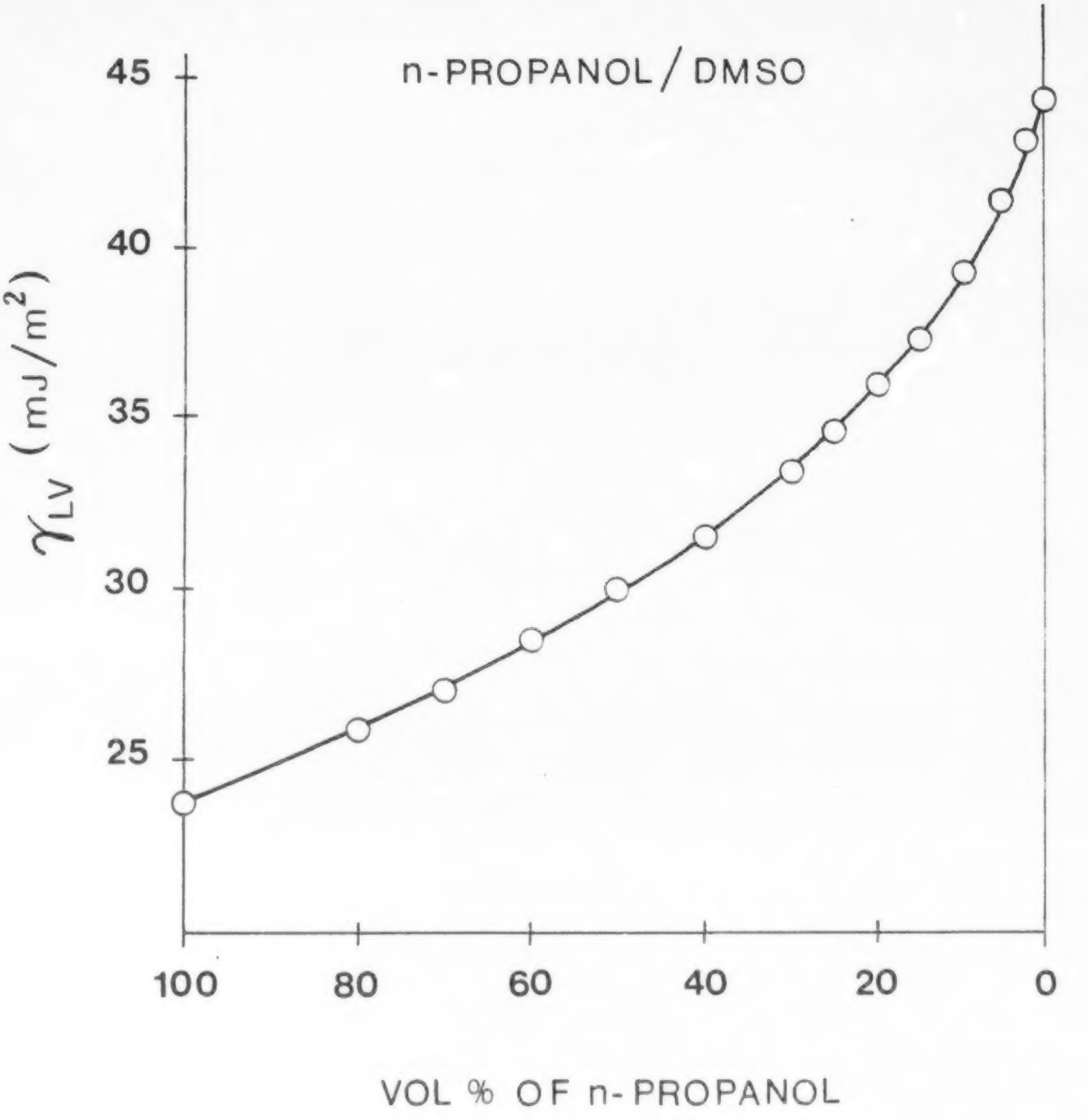


Figure 16: Surface Tension, γ_{LV}, of the Liquid Mixtures of n-Propanol/DMSO versus Concentration of n-Propanol

POOR

QUALITY

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